THE JOURNAL

OF THE

American Chemical Society

VOL. LI

JANUARY—JUNE
1929

Editor
ARTHUR B. LAMB

EASTON, PA.
MACK PRINTING COMPANY
1929

The Journal of the American Chemical Society

VOL. 51 JANUARY, 1929 No. 1

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

A VACUUM TUBE POTENTIOMETER FOR RAPID E.M.F. MEASUREMENTS[1]

BY H. M. PARTRIDGE

RECEIVED MARCH 24, 1928 PUBLISHED JANUARY 8, 1929

Applications of one or more triode valves to various forms of apparatus suitable for the determination of PH values, electrode potentials, electro-titrations and the like have been described by several writers.[2] Nearly all of these require a calibration of the valves, are dependent upon the constancy of the characteristics of the valves and require sources of filament and plate potentials which will not vary over a considerable period of time. These limitations have been the motive for the development of the apparatus herein described and which has the following attributes: (a) it is a direct reading, no current device; (b) it is independent of the characteristics of the valves and of their power supply; (c) the "balance" condition is definite and very stable; (d) since the e.m.f. is read directly from a voltmeter in the grid circuit of the first (four element) tube, the values obtained will be dependent on the precision of this meter; (e) the maximum current taken from the cell is of the order of 10^{-9} ampere—at "balance" it is 0. The unknown cell may, therefore, be left continually in circuit during the balancing, which requires only a single operation; (f) the resistance of the cell under measurement is unimportant. No difficulty has been experienced in measuring the e.m.f. of a cell containing two glass electrodes; (g) when used with a cell containing properly prepared electrodes, PH values may be rapidly determined and are reproducible to 0.02 of the Sorensen unit.

Principle of Operation

In place of the conventional "bridge" a vacuum tube amplifier consisting of a tetrode and a triode is substituted. For a more complete descrip-

---

[1] Presented at the Fall Meeting of the American Chemical Society held at Swampscott, Massachusetts, September 13, 1928.

[2] Van der Bijl, "The Thermionic Vacuum Tube," McGraw-Hill Book Co., Inc., New York, 1920; Goode, THIS JOURNAL, 44, 26 (1922); 47, 2483 (1925); Fitch, J. Opt. *Soc. Am.*, 14, 348 (1927).

tion of the operation of the valves than will be attempted here, the reader is referred to a text on wireless communication or to the articles by Goode. Several of the more common types of broadcast receiver tubes can be adapted to this work, but after a study of the characteristics of different audions, the types "—22" and "—20" were, respectively, selected. A of Fig. 1 shows the mutual conductance curve for the "—22" type of valve.

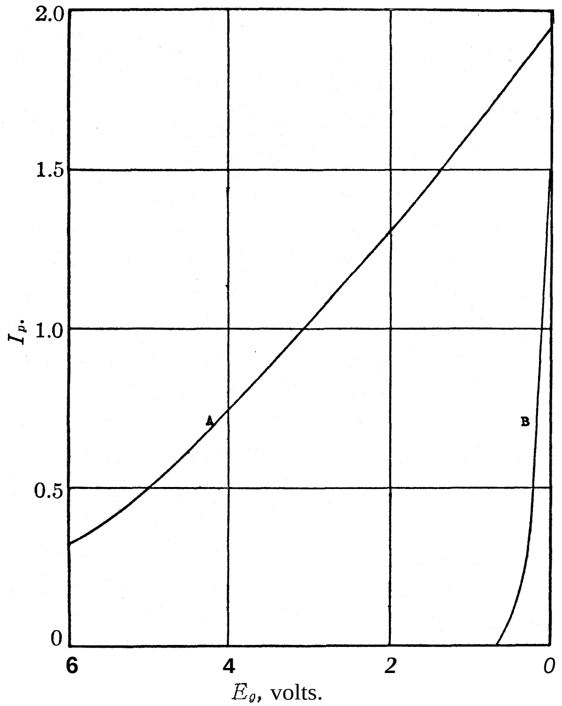


Fig. 1.

A—Grid voltage–plate current characteristic for shielded plate valve, plate voltage = **135** volts; outer grid voltage = 45 volts; inner grid voltage = E_g. B—Grid voltage–plate characteristic of vacuum tube potentiometer. E_g = potential applied between inner grid and filament of tetrode. I_p = plate current of triode in milliamperes.

The inner grid of the four element tube is used as the control grid. The outer grid is made positive with respect to the filament by 45 volts. The plate is operated at a potential of 135 volts. If the inner grid of this tube is connected directly to the negative lead of the filament, the resulting grid voltage is zero and a glance at the curve shows that the plate current under these conditions is 1.95 milliamperes. If now a cell with an unknown e.m.f. is connected between inner grid and filament with the negative side toward the grid, an unknown negative grid voltage results and the plate current drops to some lower value. An extremely feeble current will, under these conditions, be drawn from the cell being measured. A source of variable potential supplied by a dry cell or a storage cell and spanned by a voltmeter is inserted in the grid-filament circuit in such a manner that the variable potential opposes the unknown e.m.f. The variable potential is altered until the plate current again becomes 1.95 milliamperes. The unknown cell is now giving no current and the true e.m.f. of the cell may be read directly from the voltmeter. The measurement is also independent of the characteristics of the valve since the initial and final plate current values are identical, and are represented by a single point on the mutual conductance curve. The assumption is made, of course, that the tube characteristics and batteries have remained constant during the minute or so which has been spent in taking the readings. As a precautionary measure, a simple switch is provided by which the operator may, in a few seconds, check the plate current value before and after each reading. A more complete description of this procedure will be found elsewhere in the paper.

Actually, two valves are employed in such a manner that the variation in plate current of the tetrode is amplified by the triode. Curve B of Fig. 1 shows this change in plate current in the triode with accompanying variation of grid potential at the tetrode. The increased sensitivity of this arrangement over that of a single tube is apparent by contrasting the slopes of the two curves of Pig. 1. Obviously the actual principle of operation is the same as if a single tube were used.

Apparatus and Circuit Constants

The circuit employed is shown in Fig. 2. The filaments of both tubes are heated by battery A, which consists of three ordinary lead storage cells. **A** 20-ohm rheostat F regulates the potential applied to the filaments, which should be operated at *3.3* volts for maximum useful life and efficiency. The plates of the valves are supplied from batteries B_1, B_2 and B_3, which may be "B" batteries of the type used for broadcast reception and having values of 45, 22.5 and 67.5 volts, respectively. Storage cells may be used if preferable but they must be kept free from dust and charging spray or troublesome leakage will result. The plate current of the triode is registered on the milliammeter MA, which should have a full-scale deflection for 1.5 milliamperes. The absolute precision of this instrument is of secondary importance since no direct readings of the plate current need be taken. Coupling resistance R is a 100,000-ohm wire-wound resistance of the cartridge type having a small temperature coefficient and capable of dissipating 0.75 watt. The apparently large power rating of this resistance is specified to make certain that there is no rise in temperature due to the plate current of the tetrode, which it is continually required to pass.

If the grid and filament of the tetrode are connected together, the magnitude and direction of the current through resistance R is such that too great a negative potential is applied to the grid of the triode to allow any plate current to flow through MA. In order that MA may show full-scale deflection, the grid of the tetrode will have to be negative with respect to its filament by a value between two and three volts. This is accomplished by the 400-ohm "potentiometer" C with its winding spanning resistance F. The values selected for the source of the opposing potential O, for the voltage divider D and for the voltmeter V will depend upon the e.m.f. of the cell E which is to be measured. For values up to six volts, D also may be a good grade "potentiometer" of the broadcast receiver type. For all PH work and for most work in determining electrode potentials, the opposing battery O may be a single dry cell or a storage cell. The choice of the voltmeter V will depend upon the range of voltage to be covered and the accuracy desired. The writer has found the Weston Model I "Electrolysis Voltameter" with its five voltage ranges a very useful instrument, although some other types of meter are capable of a little better precision. The switch S is of the single pole double-throw type with its blade connected to the grid as shown in Fig. 2.

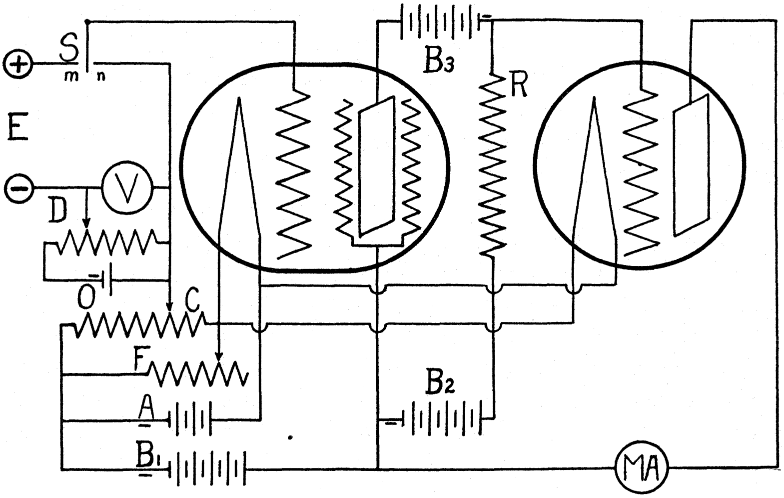


Fig. 2.—Diagram of connections.

Operation

If the circuit has been properly connected, the milliammeter MA should read zero when the switch S is thrown to position n and the slider arm of C is in such a position that it is directly connected with the filaments of both valves. If the slider arm of C is cautiously advanced toward the battery end of the winding, a point will be found at which MA will register nearly 1.5 milliamperes. If the cell E whose e.m.f. is to be measured has been attached in the proper manner and with the switch S connecting it to the circuit at m, the reading of MA is reduced in magnitude. The switch S is now thrown to n so that it connects grid and filament directly through C and the reading on MA noted. For convenience C may be adjusted until the needle of the milliammeter is exactly coincident with a marked value on the scale, for example, 1.4. The switch S is returned to its former position, m, and voltage divider D is advanced until the triode plate current has reached its former value, 1.4. Care should be taken not to force the plate current meter off the scale lest it be damaged. The reading on the voltmeter V at this point registers the e.m.f. of cell E.

Advantages

The device described herewith is somewhat more convenient than most vacuum tube potentiometers for chemical measurements in that the valves do not have to be calibrated and it is not essential that their characteristics remain constant over long periods. It is considerably more rapid than the average potentiometer in that only one adjustment is necessary for one measurement. Owing to the conditions under which the device is operated, the maximum current taken from the cell is exceedingly small. It may be used for the measurement of a cell whose internal resistance is too great to allow it to be measured by a potentiometer employing the conventional Poggendorf system. Glass electrodes furnish such an example. W. S. Hughes[3] has found that the average glass electrode made from soft glass has a resistance of between 23 and 100 megohms. In this connection curves are given in Figs. 3 and 4 plotted from data obtained in neutralization titrations employing glass electrodes. Fig. 3 is an HCl–NaOH ti-

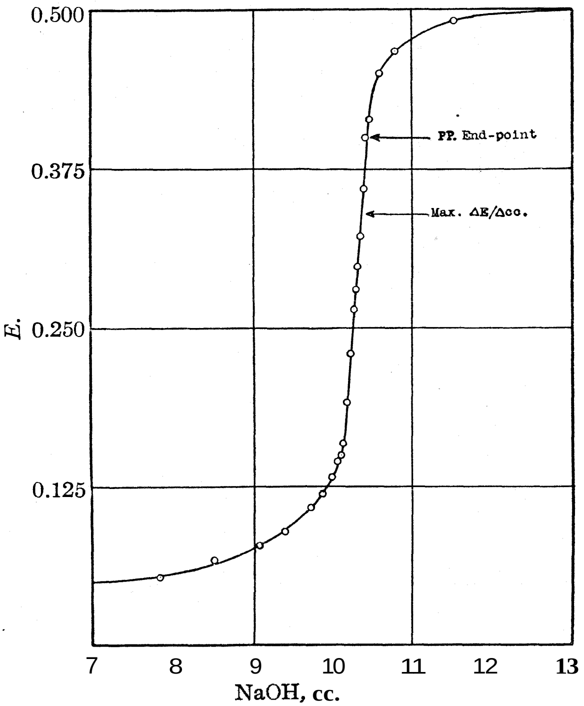


Fig. 3.—Neutralization of hydrochloric acid.

---

[3] Hughes, This Journal, 44, 2860 (1922).

tration employing one calomel and one glass electrode. Fig. 4 represents an NaOH–acetic acid neutralization in a cell containing two glass electrodes. While the points in the latter case do not represent a curve remarkable for its smoothness, they were obtained under conditions of extreme atmospheric humidity and electrical disturbances which would make the electrometer, ordinarily used for glass electrode measurements, quite useless.[4] For a more complete discussion of the glass electrode the reader is referred to papers by Watson and others.[3,5]

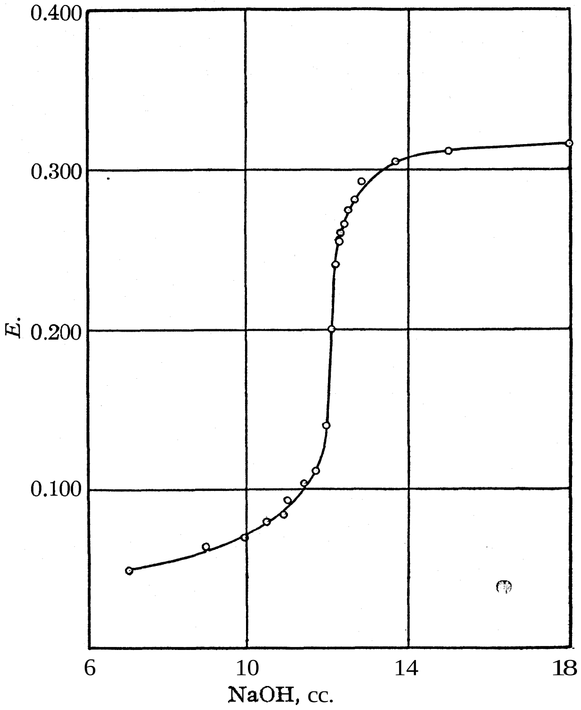


Fig. 4.—Neutralization of acetic acid—cell containing two glass electrodes.

Precautions

No trouble should be experienced from leakage if the apparatus is used on a dry wooden table. If, however, it is desirable to employ the potentio-

---

[4] If greater accuracy is desired than can be obtained with a voltmeter, V, D and O of Fig. 2 may be substituted by a potentiometer connected in such a manner that a known potential opposes E. If MA has 150 scale divisions for 1.5 milliamperes, an accuracy of 0.00015 volt will be obtained.

[5] Watson, *Chem. Eng. Mining Rev.*, 20, 59-62 (1927); Kerridge, *Biochem. J.*, 19, 611 (1925); *J. Sci. Instruments*, 3, 404 (1926); Bayliss, Kerridge and Conway-Verney, *J. Physiol.*, **61**, 448 (1926); Brown, *J. Sci. Instruments*, 2, 12 (1924); v. Steiger, *Z. Elektrochem.*, 30, 259 (1924); Horowitz, *Z. Physik*, 15, 369 (1923).

meter on a stone-topped table or upon one which has at some time been bespattered with reagents, careful insulation of all batteries from each other and from the table will be necessary. All wiring should be done so that conductors do not touch one another even though they carry "insulation." The cell E to be measured should be placed upon a dry hardwood board, hard rubber or other insulating material. Due to the high amplification obtained, the valves should he kept as free as possible from mechanical vibration. The inner grid of the tetrode should be connected with flexible wire. In some instances connecting the negative side of the filaments to earth may be helpful although in all work done by the writer this has been found unnecessary.

Summary

A device has been described which employs a tetrode and a triode in a simple potentiometer circuit and arranged in such a manner that calibration of the valves and the constancy of their characteristics are unnecessary. Since the apparatus is essentially electrostatic in operation, it is particularly adapted to the measurement of cells having high internal resistance. As only one adjustment is necessary, measurements may he made with comparative rapidity.

NEW YORK CITY

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 481

THE SYNTHESIS OF WATER WITH A SILVER CATALYST. II. ENERGY OF ACTIVATION AND MECHANISM

BY ARTHUR F. BENTON AND JOSEPH C. ELGIN

RECEIVED MAY 10, 1928 PUBLISHED JANUARY 8, 1929

Introduction

In a number of examples of homogeneous, bimolecular gas reactions it has been shown[1] that the absolute rate of reaction may be expressed by the equation

$$-\frac{dC}{dt} = Ze^{-\frac{E}{RT}}$$

where C is the concentration of the reacting species at time t, Z is the number of collisions in unit time per unit of volume, and E is the energy of activation per two moles of reactant. $e^{-E/RT}$ is, therefore, the fraction of the total number of collisions which is effective. Since the fraction of the molecules which have energy of any particular kind, kinetic, rotational, vibrational or electronic, in excess of E calories per mole is also approxi-

[1] Lewis, J. Chem. *Soc.*, 113, 471 (1918); Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926, pp. 50 *et seq.*

mately equal to $e^{-E/RT}$, it has been concluded that all collisions are effective in which at least $E/6.06 \times 10^{23}$ cal. of energy of an appropriate kind are available in the two colliding molecules.

The corresponding hypothesis suggests itself for the rate of reaction between two gases in contact with a solid catalyst, particularly for those cases in which only one of the reactants is adsorbed. It has not been possible to test such an assumption hitherto because catalytic studies have seldom been accompanied by the necessary adsorption measurements, and in the few cases in which these have been carried out it has usually been found that both reactants are adsorbed.[2] While it is conceivable that the hypothesis might be applicable to cases of the latter kind, adequate data are not available on the general problem of adsorption in mixtures.

In a previous paper[3] it was shown that the combination of hydrogen and oxygen in contact with metallic silver is a convenient example for experimental test, since under the conditions employed silver strongly adsorbs oxygen but does not take up hydrogen in measurable quantity. The rate of reaction was found to be proportional to the pressure of hydrogen, independent of the oxygen pressure and markedly retarded by water vapor. Since the oxygen adsorption is nearly independent of the pressure, these results are evidently in qualitative agreement with the hypothesis that the reaction mechanism depends on collisions of gaseous hydrogen molecules with those parts of the surface which are covered by adsorbed oxygen but free from adsorbed water. Since the previous work did not include measurements of the adsorption of water vapor, it was not possible to test the hypothesis quantitatively.

The necessary adsorption measurements have now been carried out on a new silver catalyst and the reaction kinetics have been redetermined for this new sample at two temperatures. The results are found to be in agreement with the hypothesis that reaction occurs at every collision of hydrogen with "dry" adsorbed oxygen in which the total energy available on collision exceeds the true energy of activation.

Apparatus and Procedure in Kinetic Experiments

The apparatus and procedure were the same as those employed previously,[3] with one exception. It was feared that when the hydrogen–oxygen mixtures entered the catalyst dry, as in the earlier work, the greater freedom from adsorbed water at the entering end of the catalyst would lead to so great an evolution of heat due to reaction at this point

---

[2] See, for example, the extensive studies by Pease and collaborators on the combination of ethylene and hydrogen in contact with various metals, THIS JOURNAL, 45, 1196, 2235, 2296 (1923); 47, 1235 (1925); 49, 2503, 2783 (1927).

[3] Benton and Elgin, THIS JOURNAL, 48, 3027 (1926).

that even the high thermal conductivity of silver might be insufficient to prevent a considerable temperature gradient in the catalyst. For this reason the present experiments were carried out with a constant concentration of water vapor in the enteriog gases, amounting to approximately 10% by volume.

The introduction of this water vapor was accomplished by adding the desired quantity of hydrogen to the oxygen stream, or *vice* versa, and passing the mixture over heated platinized asbestos or copper oxide.[4] The mixture of oxygen and water vapor thus produced, after uniting with a current of hydrogen in the desired proportion, was passed downward over the silver catalyst. All tubing through which water vapor passed was heated externally by passing an electric current through coils of chromel wire in order to avoid condensation. The total rate of flow of the gas mixture entering the catalyst was in all cases 50 cc. per min. (0°, 760 mm.).

The silver catalyst was obtained from another sample of the silver oxide previously employed and the reduction with hydrogen at low temperature was carried out in the manner already described, the final temperature being 100°. Preliminary experiments with the catalyst thus prepared showed that the activitv was inconveniently high, since hydrogen–oxygen mixtures were exploded when passed over it at room temperature. It was therefore heated in hydrogen at 310° for four hours to reduce its activity to a suitable value. The mass was cylindrical in shape, 3 cm. in diameter and approximately 5 cm. high, giving an apparent volume of 35 cc. The weight was 47.70 g.

The method of procedure was the same as previously reported. To avoid possible uncertainties due to previous history, the catalyst was given a uniform treatment before every experiment, consisting in heating in hydrogen at 96° for one hour. Check runs were made alternately throughout the investigation. Correction for the small changes in activity which were thus observed was made by adding to, or subtracting from, the yield in each run the percentage amount per run necessary to bring the checks into agreement.

Results of Kinetic Experiments

The results of the experiments on reaction kinetics are given in Table I in the order in which they were made. The values for the observed yields, in the next to the last column, represent the net water formation after subtracting the 20.2 mg. per five minutes present in the entering gas.

The values in Cols. 5 and 6 were calculated as follows. The pressure of hydrogen in the entering gas is V_HP/V, where V_H and V are the volumes (at 0°, 760 mm.) of hydrogen and total gas, respectively, entering the catalyst per five minutes and P is the corrected barometric pressure.[5] The hydrogen pressure in the exit gas is

$$\frac{V_{\mathrm{H}} - \frac{22.4}{18}\,Y}{V - \frac{11.2}{18}\,Y}\,P$$

---

[4] Copper oxide was found preferable to platinized asbestos, as the use of the latter occasionally led to mild explosions.

[5] The pressure drop in the catalyst bed was negligible at a rate of flow of 50 cc. per min.

TABLE I

REACTION KINETICS

Total flow, 50.0 cc. per min. (0°, 760 mm.). Water in entering gas 20.2 mg. per 5 min. Excess oxygen.

Run	Temp., °C.	Ent. H, cc. per min.	Barometer, mm. at 0°	Av. H press., mm.	Av. water press., mm.	Yield, mg. of water per 5 min.		
						Calcd.	Obs.	Corr. for activity
10	94	10.04	744.9	139.1	88.1	40.4	6.2	7.8
11	108	10.04	749.1	123.7	105.6	40.4	15.2	18.3
12	94	10.04	747.2	138.5	88.7	40.4	6.8	7.8
13	108	2.51	750.0	29.0	84.0	10.1	4.7	5.1
14	94	10.04	748.8	137.6	90.3	40.4	7.5	7.8
15	108	5.02	748.5	59.2	92.1	20.2	8.8	9.0
16	94	10.04	750.0	137.3	91.0	40.4	7.8	7.8
17	108	17.57	749.1	219.0	131.1	70.7	26.8	26.9
18	94	10.04	747.6	137.0	90.5	40.4	7.7	7.8
19	108	25.10	746.0	321.0	148.5	101.0	34.7	34.9
20	94	10.04	744.2	136.1	90.3	40.4	7.8	7.8
21	94	2.51	741.0	32.1	78.5	10.1	2.6	2.6
22	94	10.04	742.3	135.8	90.1	40.4	7.8	7.8
23	94	5.02	745.1	66.8	83.5	20.2	4.6	4.9
24	94	10.04	746.6	138.2	88.8	40.4	6.9	7.8
25	94	17.57	747.6	245.7	95.7	70.7	10.7	12.7
26	94	10.04	748.5	139.6	87.8	40.4	6.3	7.8
27	94	25.10	750.3	354.5	105.0	101.0	14.8	17.6
28	94	10.04	748.5	138.7	88.8	40.4	6.8	7.8

where Y is the observed yield in mg. of water per five minutes. Hence the average hydrogen pressure is

$$P_H = \frac{P}{2}\left(\frac{V_H}{V} + \frac{V_H - \frac{22.4}{18}Y}{V - \frac{11.2}{18}Y}\right)$$

Similarly, the average pressure of water vapor (P_W) has been calculated from the expression

$$P_W = \frac{22.4}{18}\cdot\frac{P}{2}\left(\frac{20.2}{V} + \frac{20.2 + Y}{V - \frac{11.2\,Y}{18}}\right)$$

An attempt was made (Runs 5 and 9) to use mixtures containing an excess of hydrogen, but such experiments were always followed by a permanent decrease in catalytic activity. This effect is probably attributable to the fact that at the higher rates of reaction obtained with excess hydrogen, the catalyst surface is kept comparatively free from adsorbed oxygen with the result that local overheating causes a sintering of the active surface.

An earlier series of kinetic experiments was carried out with another catalyst, using 10 mg. of water per five minutes in the entering gas. The results are omitted because an explosion destroyed the catalyst before its adsorptive power had been determined. The general character of the results is similar to those in Table I, and the data are fitted by the same type of kinetic equation.

Apparatus and Procedure in Adsorption Experiments

The amount of oxygen adsorbed by the catalyst was determined by the static method described in the previous paper.

The adsorption of water was determined by a flow method. Mixtures of water vapor with oxygen or hydrogen in proper proportions to give the desired partial pressure were passed over the catalyst, heated in a suitable vapor bath, until equilibrium was reached. The water in the entering gas was then shut off and the water adsorbed plus that in the free space was swept out and collected in a calcium chloride weighing tube. At the conclusion of these measurements the catalyst bulb was removed from the kinetic apparatus and sealed to the apparatus used for the determination of the oxygen adsorption. After removal of the adsorbed oxygen by treatment with hydrogen the free space in the bulb and connecting capillary was determined with hydrogen, which had previously been shown not to be measurably adsorbed by a silver catalyst. Prom this measured volume the weight of water in the free space at any partial pressure could be calculated, and hence the amount adsorbed.

Results of Adsorption Experiments

When mixtures of water vapor with hydrogen are used the adsorption of water occurs on a bare silver surface, since hydrogen is not adsorbed at the temperatures in question. Under the conditions of the catalysis, however, it has been shown that the surface is largely covered with adsorbed oxygen, and it is the adsorption of water by such a surface that is

TABLE II

ADSORPTION OF WATER VAPOR BY THE CATALYST

Partial press., mm. of Hg	Total water found Mg.	Total water found Cc.	Water in free space, cc.	Water adsorbed, cc.
Series 1.	Temperature 110°.		Oxygen covered surface	
75	9.4	11.7	3.7	8.0
175	15.0	18.6	8.5	10.1
275	19.6	24.3	13.3	11.0
75	8.8	10.9	3.2	7.7
Series 2.	Temperature 100°.		Oxygen covered surface	
75	9.4	11.7	3.3	8.4
175	15.2	18.8	7.8	11.0
275	19.4	24.1	12.2	11.9
Series 3.	Temperature 100°.		Bare surface	
75	3.8	4.7	3.3	1.4
175	9.4	11.7	7.8	3.9
275	14.0	17.4	12.2	5.2

of importance in the reaction kinetics. For this reason the majority of the measurements were made with mixtures of oxygen and water vapor (Series 1 and 2, Table II). Three partial pressures of the latter gas were used, covering the range obtaining in the kinetic experiments, at each of two temperatures, 100° (boiling water) and 110° (boiling toluene). The results are shown in Table II. The volumes given are those at 0° and 760 mm. After the first three measurements in Series 1, the catalyst was transferred to a new bulb of somewhat smaller volume than the original.

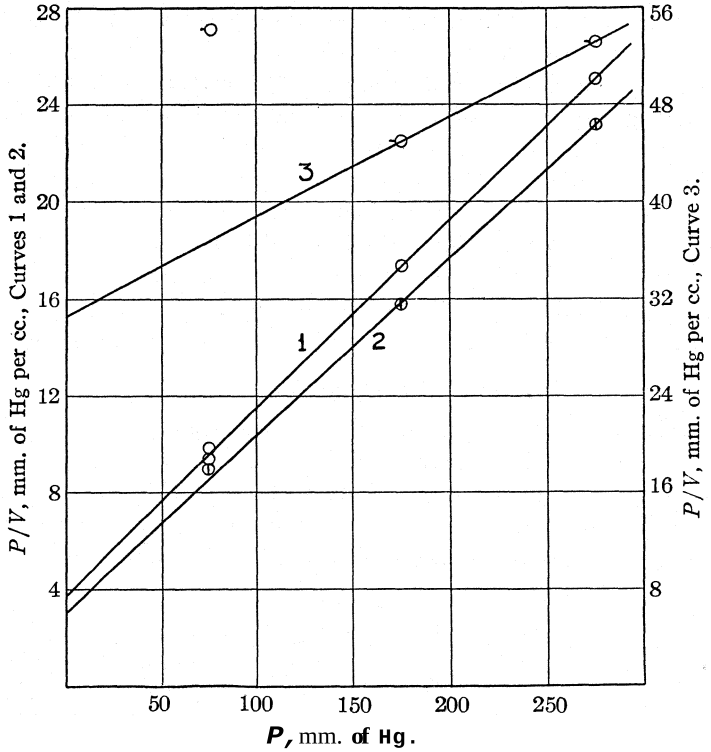


Fig. 1.—Adsorption of water vapor by the catalyst. Curves 1 and 2: oxygen-covered surface at 110 and 100°, respectively. Curve 3: bare surface at 100°.

These results are not even approximately fitted by an isotherm of the Freundlich type but agree well with the simplest form of adsorption equation derived by Langmuir[6] on the hypothesis of a unimolecular layer, namely $V = V_0aP/(1 + aP)$, where V and V_0 are the volumes adsorbed at pressure P and at infinite pressure, respectively, and a is a constant at a given temperature. This may be put in the form $P/V = 1/aV_0 + P/V_0$. A plot of P/V against P should, therefore, yield a straight line

---

[6] Langmuir, THIS JOURNAL, 40, 1370 (1918).

whose slope and intercept permit a calculation of a and V_0. The results of the three series of measurements have been plotted thus in Fig. 1. With the exception of the lowest point in Series 3, where the experimental error may be relatively great, the straight lines drawn in the figure fit the data closely. For Series 1, 2 and 3, respectively, the values of the constants are: $V_0 = 12.8, 13.7, 12.1$; $a = 0.0209, 0.0236, 0.0027$.

It may be noted that although the bare surface adsorbs much less water at a given pressure than the oxygen-covered surface, the maximum adsorptions at saturation (V_0) are nearly the same. However, the adsorption of oxygen by this catalyst at 110° was found to be 6.2 cc. (0°, 760 mm.), a value which is approximately half that obtained for water vapor.

The simplest interpretation of these facts seems to be as follows. Since the results of the previous work show that the adsorption of oxygen by silver catalyst is nearly independent of pressure and temperature over the range in question, it appears probable that this gas is taken up in a monatomic layer such that each silver atom in the surface is covered by one adsorbed oxygen *atom*. In the absence of oxygen, each exposed silver atom may take up one molecule of water, so that the volume of the latter gas adsorbed at saturation is twice as great as for oxygen molecules. When the surface is covered with oxygen, each atom of the latter can hold one molecule of water. Since the oxygen adsorption is irreversible, there can be no question of a displacement of the adsorbed oxygen by water vapor, and we conclude, therefore, that the water is held in a second layer on top of the oxygen layer.

Although in the light of previous work on adsorption by metallic catalysts the above assumption that the oxygen is taken up in a monatomic layer appears most probable, nevertheless it is obvious that other assumptions are possible, for example, that each silver atom is covered by one oxygen molecule, or perhaps that two silver atoms are required to saturate each oxygen atom. In either case the conclusions to be drawn in regard to the mechanism of the reaction between hydrogen and oxygen will not be seriously affected. This will be clear from the facts, first, that these alternative assumptions do not affect the calculations of the next paragraph on the retarding action of water vapor, because these calculations do not require a knowledge of the absolute surface of the catalyst, but only of the fraction covered by water; and, second, that the doubling or halving of the calculated absolute surface which these assumptions would require would alter the value of the energy of activation as found below by about 500 cal., which is less than the possible experimental error.

Calculation of Fraction of Surface Free from Adsorbed Water

Taking the above interpretation as substantially correct, and assuming that at the temperatures employed hydrogen is incapable of reacting with those adsorbed oxygen atoms which are covered with adsorbed water, we can calculate the retarding influence of water vapor on the reaction. If we denote by Θ the fraction of the adsorbed oxygen atoms which are covered by water under any given conditions, then $\Theta = V/V_0 = aP/(1 + aP)$. The fraction not so covered is $1 - \Theta = 1/(1 + aP)$.

If the values of a obtained in the previous section are inserted in this equation, approximate values of $1 - \Theta$ may be obtained, but it has seemed best to proceed in a somewhat different manner. From the values of V_0 already given, it is evident that the limiting adsorptive capacity for water is appreciably greater at 100° than at 110°. This probably means that as we approach a point at which the vapor is saturated, some of the adsorbed oxygen atoms become capable of taking up a second molecule of water. To overcome this difficulty, we may calculate the values of a as follows. Noting that when $\Theta = 1/2$, $a = 1/P$, and assuming as before that the total surface is measured by the 6.2 cc. of oxygen adsorbed, we may take the value of a at each temperature as the reciprocal of the pressure at which 6.2 cc. of water vapor are adsorbed. From Series 1 and 2 of Fig. 1, these values are found to be 0.0224 mm.^{-1} at 110° and 0.0284 mm.^{-1} at 100°.

From the derivation of the adsorption isotherm as given by Langmuir,[6] it may be shown that the variation of a with temperature should follow an equation of the form

$$\frac{d \log a/T^{1/2}}{d(1/T)} = \frac{Q}{4.58} = \text{constant} \qquad (1)$$

Accordingly, $\log a/T^{1/2}$ was plotted against $1/T$, and a straight line drawn through the two observed points. In this way values of a were obtained for the temperatures used in the catalysis: 0.0233 at 108° and 0.0327 at 94°.

Calculation of Specific Reaction Rate Constant

In the earlier paper it was shown that the kinetics of this reaction in flow system follow the equation

$$Y = \frac{k \cdot P_H}{1 + aP_W} \qquad (2)$$

where Y is the rate of reaction in mg. of water per five minutes, P_H and P_W are the averages of the entering and exit pressures (in mm. of mercury) of hydrogen, and water vapor, respectively, and k is the specific reaction rate constant. Considerations outlined in another place[7] show that when, as in these experiments, the conversion does not exceed 50% no serious error is introduced by the use of these arithmetical average pressures instead of the true averages obtained by integration.

From the values of a obtained in the previous section and from the data

---

[7] Benton, *Ind. Eng. Chem.*, 19, 494 (1927).

of Table I, the values of k in Equation 2 may now be calculated. The results are given in Table III.

TABLE III

SPECIFIC REACTION RATE CONSTANTS

Temperature, 108°			Temperature, 94°		
Run	$1 + aP_W$	*k*	Run	$1 + aP_W$	*k*
13	*2.96*	*0.521*	*21*	*3.56*	0.293
15	*3.14*	.477	*23*	*3.73*	.274
11	*3.46*	.513	*24*	*3 90*	.220
17	*4.06*	.498	*25*	*4.13*	.214
19	*4.46*	.485	*27*	*4.44*	.220
	Av.,	.499		**Av.,**	.244
				Av. of last *3,*	.218

Some inconsistency is evident in the results at 94°, particularly in Runs 21 and 23, where the smallness of the observed yields involves a relatively large experimental error. For this reason the average of the last three runs at 94° is considered more reliable than the average of all five runs. With the exceptions noted, Equation 2 is satisfactorily confirmed.

Calculation of True Energy of Activation

According to Arrhenius' original formulation[8] of the effect of temperature on reaction rate, the energy of activation, E, may be calculated from the equation $k \propto e^{-E/RT}$, where R is the gas constant per mole and T is the absolute temperature. For reactions in which the rate is proportional to the collision frequency, however, a slight modification is necessary,[9] since the rate of collision is itself a function of temperature. At constant pressure the rate at which gas molecules collide with a solid surface is inversely proportional to the square root of the absolute temperature; accordingly, the variation of k with temperature should follow the equation $k \propto T^{-1/2} e^{-E/RT}$. Taking logarithms on both sides, and solving for E. we obtain

$$E = \frac{4.58 T_1 T_2}{T_1 - T_2} \log \frac{k_1 T_2^{1/2}}{k_2 T_1^{1/2}}$$

From the averages given in Table II ($T_1 = 381$, $k_1 = 0.4'3'3$, $T_2 = 367$, $k_2 = 0.218$), E is found to be 16,800 cal. per mole of water formed. If k_2 is taken as 0.244, E = 14,600. The unmodified Arrhenius equation leads to values about 250 cal. smaller.

Since measurements of water adsorption were not made on the catalyst employed in the earlier work, the true energy of activation can be calculated from the data there obtained only on the assumption that the same values of the adsorption constant, *a*, are applicable to both catalysts.

---

[8] Arrhenius, *Z. physik.* ***Chem., 4, 226 (1889).***

[9] Compare Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926, p. 100.

This assumption is not altogether unreasonable, since it does not require that equal quantities of water be adsorbed by the two catalysts, but only that the shape of the adsorption isotherms be similar at equal temperatures. On this assumption we have calculated from Equation 1 values of a for the original catalyst at the temperatures used, and have employed these to determine the reaction rate constants, k, and the energy of activation. From the data of Tables I and VI of the earlier paper, E is found in this way to be 15,900 (Table I), 16,100 (Table VI, First Series) and 15,600 (Table VI, Second Series).[10]

From a consideration of these several calculations, we may take the value of the energy of activation obtained from the temperature coefficient as 16,000 cal., with an uncertainty of perhaps 1000 cal.

Test of Collision Mechanism of Reaction

On the basis of the proposed mechanism, every collision of gaseous hydrogen with adsorbed oxygen, which is free from adsorbed water, should be effective, in which the total energy available in the collision exceeds the energy of activation, E. In the previous paper it was shown that the rate of collision (R) of hydrogen with the surface, expressed in terms of the equivalent milligrams of water per five minutes, is

$$R = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot S \cdot P_H$$

where S is the area, in sq. cm., of the surface occupied by adsorbed oxygen. If we denote by f the fraction of these collisions which are effective, it is evident that the specific reaction rate constant, k, is given by the equation

$$k = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot S \cdot f \qquad (3)$$

If the energy of activation is furnished entirely by the impinging hydrogen or entirely by the adsorbed oxygen, or however it may be distributed between the two, the fraction of the collisions in which the total energy available is in excess of E is given approximately by the expression $e^{-E/RT}$

The surface area S which is occupied by oxygen may readily be calculated on the assumption that the adsorption of this gas represents a monatomic layer in which a single oxygen atom is attached to each adsorbing silver atom. The argument in favor of this assumption has been given in a previous section. On this basis, the 6.2 cc. (0°, 760 mm.) of oxygen adsorbed by the catalyst represents a surface containing 3.4×10^{20} silver

---

[10] In the earlier paper it was stated incorrectly that the observed energy of activation would necessarily be reduced when corrected for the change of water adsorption with the temperature. This statement overlooked the fact that the higher partial pressure of water vapor corresponding to the increased yields at the higher temperature may more than counterbalance the decrease in the constant a.

atoms. Since the molecular volume of silver is 10.3 cc., each silver atom occupies 1.70×10^{-23} cc., and the area assignable to each atom in the surface is $(1.70 \times 10^{-23})^{2/3}$, or 6.6×10^{-16} sq. cm. Hence the adsorbing surface of the catalyst is 2.2×10^5 sq. cm.

Inserting this value of S in Equation **3,** we obtain

$$k = \frac{4.9 \times 10^{10}}{\sqrt{T}} e^{-\frac{E}{RT}}$$

From this equation, with E taken as 16,000 cal., the calculated values of k are 1.9 at 108° and 0.88 at 94°, which may be compared with the experimental values of 0.50 and 0.22, respectively. Owing to the exponential form of the equation, however, a better comparison may be obtained by inserting the observed values of k, and calculating E. In this way E is found to be 16,900 cal. The discrepancy between the two values of E is probably within the possible limit of experimental error.

It may be mentioned that the value of the surface area employed in this calculation is certainly too large. Measurements reported in the previous paper showed that while at least half of the oxygen adsorption occurs practically instantaneously, the remainder of the gas is taken up with great slowness, so that the quantity of oxygen actually on the surface during a catalytic experiment must be less than the amount present when adsorption equilibrium has been established. From a consideration of the relative rates at which oxygen is adsorbed and removed by reaction with hydrogen it appears that the quantity actually present on the surface during the catalysis was only about half as great as the value found in the adsorption measurements. When the new value of S thus obtained is employed in Equation 3, the value of E calculated from either of the observed values of k is 16,400 cal.

Conclusion

Although the results confirm the hypothesis that reaction occurs at every collision of hydrogen with "dry" adsorbed oxygen, in which the energy available on collision exceeds the energy of activation, no information is furnished as to the proportion in which this energy is contributed by each of the reacting species, or the kinds of energy involved. If the hydrogen must be in an exceptional energy state, this energy is presumably either kinetic or rotational or both, since the specific heat at the temperatures in question shows the absence of vibrational energy, and electronic excitation is precluded by the small magnitude of the energy of activation observed.

The theory of the catalytic surface proposed by Taylor[11] postulates that the surface of a typical catalyst is composed of atoms of widely

---

[11] **Taylor,** *Proc. Roy. Soc., London,* **108A, 105 (1925).**

varying catalytic activity. If this view is correct in the case of silver, it would follow that collisions of hydrogen with oxygen adsorbed on the most active parts of the surface would be much more effective than elsewhere. Thus the energy of activation calculated from the observed reaction rates would represent a statistical average taken over the whole surface, varying from very small energies of activation for the most active spots to very high energies for the least active spots. The energy of activation calculated from the temperature coefficient of the reaction rate would represent a similar average, since the activity of the relatively inactive spots must increase more rapidly with temperature than the activity of those which are already more active. Hence it would appear that, while the results of this investigation do not lend any additional support to the theory of active spots, they can probably be satisfactorily reconciled with it.

Summary

An earlier study of the rate of combination of hydrogen and oxygen in contact with a silver catalyst has been in part repeated and extended to include measurements of the adsorption of all the gases concerned. The principal results are as follows.

1. Hydrogen is not measurably adsorbed by the catalyst under the conditions employed but oxygen is strongly adsorbed and to an extent nearly independent of temperature and pressure. The effective surface area of the catalyst has been calculated from the oxygen adsorption, on the assumption that the latter represents a monatomic layer.

2. Water vapor is somewhat adsorbed by a bare silver surface but much more strongly when the surface is already occupied by adsorbed oxygen. The results follow adsorption isotherms of the Langmuir type and permit a calculation of the fraction of the surface free from adsorbed water under the conditions of the catalysis.

3. The rate of the reaction is found to be independent of the pressure of the oxygen but proportional to the hydrogen pressure and to the fraction of the surface free from adsorbed water. The true energy of activation, obtained from the temperature coefficient, is 16,000 cal., with an uncertainty of about 1000 cal.

4. It has been found that the absolute rate of reaction agrees with that calculated on the hypothesis that reaction results from every collision of gaseous hydrogen with "dry" adsorbed oxygen in which the total energy available on collision exceeds 16,400 cal. Since these two values of the energy of activation differ by less than the experimental error, the hypothesis is considered to be confirmed for this particular reaction.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 208]

AN EQUATION OF STATE FOR GASEOUS MIXTURES. I APPLICATION TO MIXTURES OF METHANE AND NITROGEN

BY JAMES A. BEATTIE

RECEIVED MAY 16, 1928 PUBLISHED JANUARY 8, 1929

1. Introduction

Recently a new equation of state has been proposed by O. C. Bridgeman and the author[1] and applied to the compressibility data on the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane and ethyl ether. The measured pressures were reproduced over the experimentally measured temperature range and for a wide range of densities with an average deviation of 0.18% for all ten gases. This equation of state is

$$p = \frac{RT(1-\epsilon)}{V^2}[V+B] - \frac{A}{V^2} \qquad (1)$$

where A $= A_0\,(1 - a/v)$; $B = B_0\,(1 - b/v)$; $\epsilon = c/VT^3$; R is the gas constant and A_0, a, B_0, b and c are constants whose values depend upon the kind of gas under consideration.

In the present paper this equation is applied to the comprehensive set of data taken by Keyes and Burks on mixtures of methane and nitrogen, by the use of a simple rule for the calculation of the values of the constants of the mixture from those of the pure component gases. The agreement between the observed and calculated pressures is good and leads to the expectation that the method used for the calculation of the values of the constants in the case of the methane and nitrogen mixtures will also apply to other gaseous mixtures.

In his treatment[2] of binary systems, van der Waals assumed that the equation of state of a gaseous mixture was of the same general form as that for a pure gas, *i. e.*

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

He suggested that the value of the b constant for a mixture of two gases could be calculated by "linear combination" of the b values for the pure gases

$$b_x = b_1\,(1-x) + b_2x$$

where x is the mole fraction of the second component. However, through-

---

[1] Beattie and Bridgeman, THIS JOURNAL, 49, 1665 (1927); *ibid.*, **50**, 3133, 3151 (1928). A comprehensive treatment of the equation of state and a detailed comparison with the compressibility data are given in Proc. *Am. Acad. Arts Sci.*, **63**, 229 (1928).

[2] Van der Waals, "Die Continuitat des Gasformigen und Flussigen Zustandes," Part II, Barth, Leipzig, 1900.

out his book van der Waals employed the relation deduced from kinetic theory by Lorentz[3]

$$b_x = b_1(1-x)^2 + 2\,b_{12}x(1-x) + b_2x^2$$

in which

$$b_{12} = \left(\frac{1}{2}\sqrt[3]{b_1} + \frac{1}{2}\sqrt[3]{b_2}\right)^3$$

If, however, b_{12} can be represented as the average of b_1 and b_2

$$b_{12} = (b_1 + b_2)/2$$

the Lorentz equation for b_x reduces to the linear combination rule of van der Waals.

For the cohesive constant van der Waals used the relation

$$a_x = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2$$

a_{12} being an interaction constant which cannot in general be calculated from a_1 and a_2.

Galitzine[4] applied an equation of the Clausius type to Andrews'[5] data on mixtures of nitrogen and carbon dioxide and calculated the interaction constant by the relation $a_{12} = \sqrt{a_1a_2}$; the complete expression for a_x becoming

$$a_x = a_1(1-x)^2 + 2\sqrt{a_1a_2}\,x(1-x) + a_2x^2$$

or

$$\sqrt{a_x} = \sqrt{a_1}(1-x) + \sqrt{a_2}\,x$$

i. e., the square root of the a constant is linearly combined. He also used the same method of combination for the b constant,

Somewhat later D. Berthelot[6] proposed that in the application of van der Waals' equation to binary mixtures, the parameters b_x and $\sqrt{a_x}$ for the mixture be obtained by linear combination of the b and $\sqrt{a}$ constants of the component gases. This method was criticized by van der Waals,[7] who believed than in general the properties of a mixture cannot be calculated from those of the component gases, because a_{12} cannot be obtained from the constants of the pure gases. This view is also held by Happel,[8] who shows that a_{12} cannot be calculated from a_1 and a_2 unless some assumption is made regarding the law of the attractive force between the unlike molecules of the gas mixture.

Trautz and Emert[9] have measured the increase in pressure resulting from mixing two gases for many binary systems at about one atmosphere

[3] Lorentz, *Wied. Ann.*, 12, 127, 660 (1881).

[4] Galitzine, *ibid.*, 41, 770 (1890).

[5] Andrews, *Phil. Trans. Roy. Soc., London*, **178A**, 45 (1887).

[6] D. Berthelot, *Compt. rend.*, 126, 1703, 1857 (1898).

[7] Van der Waals, *ibid.*, 126, 1856 (1898). Later this criticism, which was founded on the critical behavior of gas mixtures, was for the most part withdrawn (*cf.* "Continuitat," Vol. II, p. 156).

[8] Happel, *Ann. Physik*, 26, 95 (1908).

[9] Trautz and Emert, *Z. anorg. allgem. Chem.*, 150, 277 (1926).

and at several temperatures. They computed the values of a and b of the van der Waals' equation for the pure gases at each temperature by means of van Laar's[10] temperature functions. The constants for the mixtures were obtained from these values, using the Lorentz method of combination for b, and the Galatzine–Berthelot method for a. The experimental results were explained reasonably well, although not within the experimental error.

Keyes and Burks[11] have presented a series of measurements on mixtures of methane and nitrogen and have treated these data by means of the Keyes equation for a non-associating gas

$$p = \frac{RT}{V - \beta e^{-\alpha/V}} - \frac{A}{(V + l)^2}$$

They found that the values of the constants obtained by passing an equation of state through the compressibility data on the mixtures could be calculated from the constants for the pure gases and the compositions of the mixtures when each of the constants R, β, α, $\sqrt{A}$, 1, was combined linearly.

Dalton's law of the additivity of pressures at constant volume and temperature has been the basis of much of the treatment of gas mixtures, although this principle has long been known to hold only approximately for real gases. Amagat,[12] from a study of his measurements of the compressibility of oxygen, nitrogen and air to 3000 atmospheres, found that at constant temperature and pressure the pV product for air could be obtained by linear interpolation between the pV products of the pure gases. Since the pressure is the same throughout, this rule states that the volume of a gas mixture is given by the sum of the volumes of the component gases, each measured under the total pressure of the mixture. In this form, the Amagat law of the additivity of volumes at constant pressure and temperature was studied by Leduc,[13] who claimed that it was quite exact for mixtures of the permanent gases. Penning[14] has used the exactness of this relation for air as a test of the accuracy of his measurements, and Holborn and Otto[15] have employed the rule to calculate the compressibility of pure neon from measurements on a neon–helium mixture containing 28% of helium. Keyes and Burks[11] have shown that the Amagat law is a better approximation than Dalton's

---

[10] Van Laar, "Die Zustandsgleichung von Gasen und Flussigkeiten," L. Voss, Leipzig, 1924.

[11] Keyes and Burks, THIS JOURNAL, 50, 1100 (1928).

[12] Amagat, *Ann. chim. phys.*, *[5]19*, *384* (1880); *Compt. rend.*, 127, 88 (1898).

[13] Leduc, *Compt. rend.*, 126, 218 (1898). The Amagat law is sometimes called Leduc's law, *cf.*, however *ibid.*, 127, 88 (1898).

[14] Penning, *Archives Neerlandaises*, III A, 7, 172 (1923); *Comm. Phys. Lab. Univ. Leiden*, *No.* 166.

[15] Holborn and Otto, *Z. Physik*, 23, *77* (1924).

law for methane–nitrogen mixtures and the same has been found true for oxygen–argon mixtures by Masson and Dolley[16] although the reverse was the case for argon-ethylene and oxygen-ethylene mixtures. Gillespie[17] has demonstrated that the Lewis and Randall[18] rule, which can be taken as the additivity of fugacity for gaseous mixtures at constant pressure and temperature, is correct only if the Amagat law holds.

Verschoyle[19] has shown that in the isothermal expansion

$$pV = A + Bp + Cp^2$$

the constants B and C for mixtures of hydrogen and nitrogen are not linear functions of the compositions but lie on smooth curves. Lennard-Jones and Cook,[20] from a consideration of the interaction between molecules, obtain for the B coefficient of a mixture the relation

$$B'_x = B'_{11}(1 - x)^2 + 2B'_{12}x(1 - x) + B'_{22}x^2$$

in which B'_{12} arises from the interaction of molecules of unlike species. A relation for the temperature dependence of B'_{12} is deduced and compared with the experimental results, with substantial agreement.

2. Calculation of the Values of the Constants for Gaseous Mixtures

It seems reasonable to suppose that the equation of state of a given gaseous mixture would be of the same general form as that for a pure gas and that the values of the constants could be obtained from the compressibility data in the same manner as from similar data on a pure gas. Whether the constants so obtained can be computed with sufficient accuracy for purposes of thermodynamic calculation from the values of the constants of the pure gases and the composition of the mixture is a question which must be settled experimentally. In the present paper a simple method for calculating the values of the constants of a mixture is studied from the standpoint of the experimental measurements on methane–nitrogen mixtures.

Kinetic theory considerations lead in general to quadratic equations such as those deduced by Lorentz for the calculation of the equation of state constants of a binary mixture from those of the component gases. If the interaction constant (*i. e.*, b_{12} or a_{12}) can be taken as the average of the constants of the pure gases, the equation for combining the constants reduces to a linear one; while if the interaction constant can be taken as the square root of the product of the constants of the pure gases, the rule

---

[16] Masson and Dolley, *Proc. Roy. Soc., London,* **103A,** *524 (1923).*

[17] Gillespie, THIS JOURNAL, **47,** *305 (1925).*

[18] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923,** p. *226.* See also Bichowsky, THIS JOURNAL, **44,** 116 *(1922).*

[19] Verschoyle, *Proc. Roy. Soc., London,* **111A,** *552 (1926).*

[20] Lennard-Jones and Cook, *ibid.,* **115A, 334** *(1927).*

reduces to linear combination of the square roots of the constants. The former assumption is more logical when the constant contains the dimension of density to the first power and the latter when the constant contains the dimension of density squared.

It is proposed that the values of the constants of Equation 1 for mixtures can be obtained from the constants of the pure gases by linear combination for those constants in which the dimension of density is contained to the first power, namely, a, B_0, b, c and R, and by linear combination of the square root of the constant A_0, in which the dimension of density is contained to the second power.

The volume V of Equation 1 may be (a) the total volume of n moles of the mixture, (b) the volume of an average mole or (c) the volume of one gram of the mixture.

(a) When V is the volume of n moles consisting of n_1 moles of Gas 1, n_2 moles of Gas 2, etc., the rule of combination becomes

$$\begin{aligned} A_m &= (n_1\sqrt{A_{01}} + n_2\sqrt{A_{02}} + n_3\sqrt{A_{03}} + \ldots)^2 &&= (\Sigma n_1\sqrt{A_{01}})^2 \\ a_m &= n_1a_1 + n_2a_2 + n_3a_3 + \ldots &&= \Sigma(n_1a_1) \\ B_{om} &= n_1B_{01} + n_2B_{02} + n_3B_{03} + \ldots &&= \Sigma(n_1B_{01}) \\ b_m &= n_1b_1 + n_2b_2 + n_3b_3 + \ldots &&= \Sigma(n_1b_1) \\ c_m &= n_1c_1 + n_2c_2 + n_3c_3 + \ldots &&= \Sigma(n_1c_1) \\ R_m &= n_1R + n_2R + n_3R + \ldots &&= \Sigma(n_1R) \end{aligned} \tag{2}$$

where the subscript m refers to the value of the constant for the mixture, the subscript 1 refers to Gas 1, and the summation extends over all of the gases in the mixture.

(b) When V is the volume of an average mole of the mixture, the number of moles n_1, n_2, etc., of the relations given under (a) are replaced by the mole fractions x_1, x_2, . . . of the gases composing the mixture.

(c) When V is the volume of one gram, the constants are combined according to the methods given in Equation 2, the mole numbers n_1, n_2, . . . being replaced by w_1, w_2, . . . where w is the weight fraction and the values of the constants R_1, A_{01}, a_1, B_{01}, etc., are the appropriate values for one gram of the pure Gas 1.

It is now possible to write the complete equation of state for a mixture. Using for instance the relations (2) we obtain

$$p = \frac{\Sigma(n_1)RT\,(1 - \epsilon)}{V^2}\,[V + B] - \frac{A}{V^2} \tag{3}$$

where $A = (\Sigma n_1\sqrt{A_{01}})^2[1 - \Sigma(n_1a_1)/V]$, $B = \Sigma(n_1B_{01})[1 - \Sigma(n_1b_1)/V]$, and $\epsilon = \Sigma(n_1c_1)/VT^3$. When a mixture of a given composition is studied it is more convenient to calculate from Equation 2 the values of the constants for the mixture, and use these values in Equation 1, the mixture then being treated as a pure substance. When, however, the effect of a variation in composition is considered, the general equation of state of mixtures (3) or its counterpart using the mole fraction or weight fraction must be used.

3. The Virial Equation of State for Mixtures

Since the equation of state **(3)** is completely algebraic, it can be rearranged into the virial form

$$pV = \Sigma(n_1)RT + \frac{\beta_m}{V} + \frac{\gamma_m}{V^2} + \frac{\delta_m}{V^3} \tag{4}$$

where

$$\beta_m = \Sigma(n_1)RT\Sigma(n_1B_{01}) - (\Sigma n_1\sqrt{A_{01}})^2 - \left(\frac{\Sigma(n_1)R\Sigma(n_1c_1)}{T^2}\right)$$

$$\gamma_m = -\Sigma(n_1)RT\Sigma(n_1B_{01})\Sigma(n_1b_1) + (\Sigma n_1\sqrt{A_{01}})^2\Sigma(n_1a_1) - \left(\frac{\Sigma(n_1)R\Sigma(n_1B_{01})\Sigma(n_1c_1)}{T^2}\right)$$

$$\delta_m = \frac{\Sigma(n_1)R\Sigma(n_1B_{01})\Sigma(n_1b_1)\Sigma(n_1c_1)}{T^2}$$

The parameters β_m, γ_m and δ_m are algebraic functions of temperature, the mole numbers and the values of the constants of the gases composing the mixture. For a mixture of constant composition these parameters depend only on the temperature. By use of Equation 4 most of the usual thermodynamic equations can be integrated and hence many of the more important properties of gas mixtures calculated.[21]

The second virial coefficient β_m for a binary mixture can be written in the form obtained by Lennard-Jones and Cook[20]

$$B'_x = B'_{11}(1-x)^2 + 2\,B'_{12}x(1-x) + B'_{22}x^2$$

where $B'_x = \dfrac{\beta_m}{\Sigma(n_1)^2RT}$ and x is the mole fraction of the second constituent. By comparison with Equation 4, it can be seen that

$$B'_{11} = B_{01} - A_{01}/RT - c_1/T^3$$

$$B'_{22} = B_{02} - A_{02}/RT - c_2/T^3$$

$$2B'_{12} = B_{01} + B_{02} - 2\sqrt{A_{01}A_{02}}/RT - (c_1 + c_2)/T^3$$

Thus by use of the method of combining the constants given in Section 2, it is possible to calculate the value of B'_{12} from the equation of state constants of the pure gases composing the mixture and also determine its temperature variation.

4. Comparison of the Equation of State for Mixtures with the Experimental Data

It is generally true that two sets of pressure–volume–temperature data taken by different observers on the same gas do not agree with each other to the same order of accuracy as the consistency of each group of measurements within itself. Hence for a study of gas mixtures, the observations on the pure gases as well as on the mixtures should be made in the same apparatus. There exist several sets of data which fulfil this condition but in almost every case the investigator studied so few isotherms that it is not possible by a treatment of these data alone to obtain reliable constants for the pure gases.

---

[21] *Cf.* Beattie, *Phys. Rev.*, *31*, *680 (1928)*; *ibid.*, *32*, *691*, *699 (1928)*.

In the bibliography on the compressibility of gas mixtures given by Pickering,[22] the only measurements which are complete enough to test an equation of state for mixtures are those of Bartlett, which will be treated later.

Recently Keyes and Burks have measured the compressibility of methane[23] and three mixtures of methane and nitrogen[23,24] for five isotherms from 0 to 200° and for pressures extending to about 250 atmospheres. Using the same apparatus, Smith and Taylor[25] had previously measured the compressibility of pure nitrogen over the same temperature and pressure range. There is thus presented a complete series of pressure–volume–temperature data extending from pure nitrogen to pure methane covering the same temperature and pressure range. They were taken in the same apparatus using the same methods for calculating the results and hence the relative values should be very good, probably better than the absolute values.

In a previous publication,[1] the data of Smith and Taylor on pure nitrogen and of Keyes and Burks on pure methane have been considered, and the constants of the equations of state, based on these two sets of measurements alone, determined in units of international atmospheres, liter per mole and degrees Kelvin. Since all of the original **data** of these two groups of observers are in the volume unit of cubic centimeters per gram, the constants have been calculated to this basis. In Table I are given these values of the constants for the pure gases, together with those for the

TABLE I

VALUES OF THE EQUATION OF STATE CONSTANTS FOR NITROGEN, METHANE AND THEIR MIXTURES

Units: international atmospheres; cc. per gram; degrees Kelvin (**T°K.** = t°C + 273.13). Compositions are in weight fractions. The values of the constants for the mixtures are calculated from the constants of the pure gases and the compositions by means of the relations (2).

Gas	$\Sigma(w_1R_1)$	$(\Sigma w_1\sqrt{A_{01}})^2$	$\Sigma(w_1a_1)$	$\Sigma(w_1B_{01})$	$\Sigma(w_1b_1)$	$\Sigma(w_1c_1)$
Nitrogen	2.92904	1457.5	0.6382	1.5398	−0.5740	2.00 × 10^6
69.556% N_2; 30.444% CH_4	3.59572	3048.2	.7961	2.1321	− .7006	3.827 × 10^6
31.014% N_2; 68.986% CH_4	4.43974	5894.4	.9961	2.8819	− .8610	6.139 × 10^6
29.69% N_2; 70.31% CH_4	4.46873	6008.7	1.0030	2.9076	− .8665	6.219 × 10^6
Methane	5.11890	8860.0	1.157	3.4852	− .9900	8.00 × 10^6

---

[22] Pickering, "International Critical Tables," McGraw-Hill Book Co., New York, 1928, Vol. III, p. 17.

[23] Keyes and Burks, THIS JOURNAL, 49,1403 (1927).

[24] Burks, "Thesis," Massachusetts Institute of Technology, Cambridge, Mass., 1924.

[25] Smith and Taylor, THIS JOURNAL, 45, 2107 (1923); *ibid.*, **48**, 3122 (1926).

TABLE II

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR NITROGEN

For each isometric the observed pressures are given in the first horizontal line, and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

	Temp., °C.	0	49.98	100	152.34	200	Av. dev.	
Vol. cc./g.		Pressures, atmospheres					Atm.	%
23.1195	obs.	34.18	41.01	47.81	54.93	61.38		
	obs. − calcd.	0.02	0.04	0.05	0.06	0.05	0.044	0.090
20.1039	obs.	39.25	47.14	55.09	63.32	70.84		
	obs. − calcd.	0.02	0.00	0.05	0.03	0.04	.028	.050
17.0883	obs.	46.05	55.50	65.02	74.81	83.77		
	obs. − calcd.	−0.03	−0.03	0.07	0.02	0.02	.034	.056
14.0728	obs.	55.84	67.47	79.28	91.44	102.55		
	obs. − calcd.	−0.01	−0.10	0.04	0.01	0.03	.038	.052
11.0572	obs.	70.98	86.29	101.70	117.68	132.20		
	obs. − calcd.	0.00	−0.08	0.01	0.00	−0.01	.020	.022
9.0468	obs.	86.71	106.13	125.56	145.77	163.91		
	obs. − calcd.	−0.04	−0.06	0.05	0.10	−0.07	.064	,052
7.0364	obs.	111.96	138.26	164.40	191.61	216.15		
	obs. − calcd.	0.08	0.09	0.13	0.16	0.01	.094	.060
5.0260	obs.	160.22	200.15	240.05	281.96	319.53		
	obs. − calcd.	1.25	0.92	0.97	1.45	1.44	1.206	.520
Total average deviation to 5 cc./g.							.191	.113
Total average deviation to 7 cc./g.							.046	.055

TABLE III

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR METHANE

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

	Temp., °C.	0	50	100	150	200	Av. dev.	
Vol. cc./g.		Pressures, atmospheres					Atm.	%
40	obs.	32.30	39.42	46.47	53.49	60.49		
	obs. − calcd.	−0.02	0.02	0.03	0.04	0.04	0.030	0.062
35	obs.	36.51	44.76	52.94	61.04	69.16		
	obs. − calcd.	−0.04	0.01	0.04	0.02	0.04	.030	.060
30	obs.	42.00	51.81	61.51	71.14	80.75		
	obs. − calcd.	−0.05	0.01	0.03	0.03	0.02	.028	.050
25	obs.	49.44	61.50	73.45	85.26	97.05		
	obs. − calcd.	−0.06	−0.01	0.04	0.00	−0.01	.024	.040
20	obs.	60.13	75.78	91.24	106.54	121.81		
	obs. − calcd.	−0.07	−0.02	0.01	−0.02	−0.02	.028	.040
15	obs.	76.88	99.00	120.85	142.43	163.97		
	obs. − calcd.	−0.03	−0.07	−0.05	−0.12	−0.13	.080	.062
12	obs.	92.69	121.95	150.88	179.41	207.95		
	obs. − calcd.	0.15	−0.05	−0.05	−0.15	−0.06	.092	.068
10	obs.	107.95	145.08	181.84	218.12	254.27		
	obs. − calcd.	0.53	0.09	0.10	0.07	0.19	.196	.142
Total average deviation							.064	.066

mixtures calculated by the relations of Equation 2, using the weight fractions determined by analysis.

In Tables II to VI are presented the comparison of the observed pressures with those calculated from the equations of state for mixtures, and in Table VII is given a summary of the results. The "Observed Pressures" listed are the original unsmoothed values.

TABLE IV

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR A MIXTURE CONTAINING 69.556% OF NITROGEN AND 30.444% OF METHANE BY WEIGHT

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Temp, °C. Vol. cc /g.		0	50	100	150	200	Av. dev. Atm.	 %
		Pressures, atmospheres						
30	obs.	31.64	38.17	44.66	51.13	57.59		
	obs. − calcd.	0.04	0.08	0.10	0.11	0.13	0.092	0.202
25	obs.	37.76	45.71	53.63	61.51	69.38		
	obs. − calcd.	0.07	0.11	0.15	0.17	0.19	.138	,252
20	obs.	46.81	57.00	67.15	77.22	87.28		
	obs. − calcd.	0.12	0.18	0.26	0.28	0.32	.232	,340
15	obs.	61.68	75.81	89.89	103.82	117.74		
	obs. − calcd.	0.24	0.33	0.47	0.52	0.59	.430	.470
12	obs.	76.35	94.72	113.01	131.11	149.23		
	obs. − calcd.	0.40	0.54	0.76	0.88	1.07	.730	.630
10	obs.	90 95	113.86	136.64	159.25	181.66		
	obs. − calcd.	0.65	0.84	1.13	1.39	1.53	1.108	.798
8	obs.	11293	143.25	173.48	203.31	233.07		
	obs − calcd.	1.19	1.46	2.04	2.44	2.90	2.006	1.138
6	obs.	150.93	195.53	239.85	283.62	327.44		
	obs. − calcd.	2.88	3.59	4.77	5.83	7.20	4.854	2000
	Total average deviation to 6 cc./g.						1.199	0.729
	Total average deviation to 8 cc./g.						0.677	.547

TABLE V

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE ROR A MIXTURE CONTAINING 31.014% OR NITROGEN AND 68.986% OF METHANE BY WEIGHT

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Temp., °C. Vol. cc /g.		0	50	100	150	209	Av. dev. Atm.	 %
		Pressures, atmospheres						
29.9456	obs.	37.70	45.99	54.23	62.42	7059		
	obs. − calcd.	0.00	0.01	0.03	0.02	0.00	0.012	0.022
24.9456	obs.	44.66	54.81	65.04	74.92	84.91		
	obs. − calcd.	−0.01	−0.01	0.14	−0.02	−0.05	.046	.070
19.9456	obs.	54.82	67.95	80.92	93.82	106.68		
	obs. − calcd.	−0.01	0.01	−0.01	−0.05	−0.08	,032	.034
14.9456	obs.	71.11	89.48	107.71	125.79	143.70		
	obs. − calcd.	0.03	−0.05	−0.05	−0.09	−0.23	.090	.076

TABLE V (Concluded)

Vol. cc./g.	Temp., °C.	0	50	100	150	200	Av. dev. Atm.	%
		Pressures, atmospheres						
11.9456	obs.	86.97	110.90	134.73	158.57	182.03		
	obs.−calcd.	0.29	−0.09	−0.23	−0.16	−0.36	.226	.176
9.9456	obs.	102.36	132.46	162.65	192.51	222.07		
	obs.−calcd.	0.52	−0.11	−0.14	−0.20	−0.40	.274	.192
7.9456	obs.	126.04	165.87	206.42	246.51	286.10		
	obs.−calcd.	1.85[a]	0.19	0.12	0.07	−0.18	.140	.065
6.9456	obs.	143.52	191.02	239.94	288.11	335.68		
	obs.−calcd.	3.28[a]	0.74	0.81	0.79	0.57	.728	.293
	Total average deviation						.181	.113

[a] These two deviations were not included in the averages.

TABLE VI

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR A MIXTURE CONTAINING 29.69% OF NITROGEN AND 70.31% OF METHANE BY WEIGHT

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Vol. cc./g.	Temp., °C.	0	50	100	150	200	Av. dev. Atm.	%
		Pressures, atmospheres						
40	obs.	28.87	34.97	41.04	47.08	53.08		
	obs.−calcd.	0.00	0.03	0.05	0.06	0.04	0.036	0.084
35	obs.	32.75	39.81	46.82	53.80	60.74		
	obs.−calcd.	0.00	0.04	0.06	0.08	0.06	.048	.096
30	obs.	37.84	46.22	54.51	62.77	70.99		
	obs.−calcd.	0.01	0.06	0.08	0.10	0.09	.068	.120
25	obs.	44.82	55.09	65.26	75.36	85.41		
	obs.−calcd.	0.02	0.08	0.12	0.13	0.11	.092	.134
20	obs.	55.00	68.26	81.35	94.37	107.31		
	obs.−calcd.	0.06	0.14	0.18	0.20	0.19	.154	.186
15	obs.	71.30	89.91	108.28	126.48	144.61		
	obs.−calcd.	0.16	0.25	0.32	0.33	0.34	.280	.260
12	obs.	87.01	111.45	135.61	159.52	183.31		
	obs.−calcd.	0.37	0.42	0.54	0.61	0.67	.522	.392
10	obs.	102.36	133.20	163.66	193.78	223.80		
	obs.−calcd.	0.70	0.74	0.92	1.05	1.26	.934	.580
	Total average deviation						.267	.232

TABLE VII

SUMMARY OF THE AVERAGE DEVIATIONS OF THE PRESSURES CALCULATED BY THE EQUATION OF STATE FROM THE OBSERVED PRESSURES

Gas	Temp. range, °C.	Max. press., atm.	Vol. range, cc./g.	No. of points	Total av. dev. Atm.	%
N_2	0 to 200	216	23 to 7	35	0.046	0.055
69.556% N_2 + 30.444% CH_4	0 to 200	233	30 to 8	35	.677	.547
31.014% N_2 + 68.986% CH_4	0 to 200	336	30 to 7	38	.181	.113
29.69% N_2 + 70.31% CH_4	0 to 200	224	40 to 10	40	.267	.232
CH_4	0 to 200	254	40 to 10	40	.064	,066

5. Discussion of the Results

It may be well to emphasize that the values of the constants for the mixtures were calculated by means of the relations (2) from the constants of the pure gases and the composition of the mixtures, *and were not derived by passing an equation through the mixture data.*

The volume of the piezometer used in all the measurements of Smith and Taylor and of Keyes and Burks was about **13** cc., and hence for specific volumes below 7 cc. per gram the total volume of the gas was small—from 2 to 3 cc. At these large densities, a small error in the specific volume makes a large error in the pressure. Therefore, in taking the "Total Average Deviations" the two isometrics below **7** cc. per gram were not included. With this exception and two points in Table V all the measured pressures were used in taking the averages.

The equation reproduces the measured pressures for the pure gases nitrogen and methane very satisfactorily, as can be seen by an examination of Table VII. Two independent sets of measurements were made by Keyes and Burks with mixtures containing about 70% methane. The equation of state for mixtures reproduced these data with average deviations of 0.11 and 0.23%, which is again a very satisfactory result. It will be noticed that for the 70.31% methane mixture, all the deviations are positive and increase in a regular manner with the density, which could be explained by a slight error in the measured composition and hence account for the somewhat larger average deviation. The average deviation for the 30% methane mixture, which was not checked, is larger than for either of the others, being 0.55%. This could be explained on the basis of an error in the composition of the mixture, especially as the deviations are all positive and progress in a regular manner with the density. A small variation in the values of the constants A_{0m} and B_{0m} for a mixture, due to a variation in the assumed composition, will cause a large variation in the calculated pressure at the larger densities.

The question of whether or not the method of combining the constant used in the case of methane and nitrogen will prove satisfactory for other gas mixtures must be settled by further experimental work. If the equation of state constants for the two gases composing a mixture have about the same values, it may be impossible to conclude that one method of combining the constants is better than any one of several other possible methods. In the case of methane and nitrogen the B_0 constants (on a molal basis) are not so very different from each other; but for all of the ten pure gases so far treated[1] the B_0 constant does not show a wide variation (with the exception of ethyl ether). The A_0 constant for methane is about twice that for nitrogen (on a molal basis), which represents a rather wide variation. Thus it is believed that the method of combining constants used in the present paper for methane and nitrogen will hold for many other gas mixtures.

6. Summary

The equation of state proposed by Beattie and Bridgeman has been applied to mixtures of methane and nitrogen by use of a simple method for calculating the values of the constants of the mixture from those for the pure gases. The constants R, a, B_0, b and c which contain the dimension of density to the first power are combined linearly, thus $B_{0x} = B_{01}(1 - x) + B_{02}x$; the A_0 constant contains the dimension of density to the second power and hence the square root of A_0 is combined linearly, $A_{0x} = [\sqrt{A_{01}}(1 - x) + \sqrt{A_{02}}x]^2$.

It is concluded that it is possible to write a single equation by means of which pressures for the entire series of mixtures of methane and nitrogen, including the pure gases, can be calculated from the temperature, density and composition.

The satisfactory nature of the agreement between observed and calculated pressures for the mixtures of methane and nitrogen leads to the expectation that this method of combining the constants will prove applicable to mixtures of other gases. The general equation of state for mixtures is presented in Equation 3 and the virial form in Equation 4. This equation of state is completely algebraic and can be used for the integration in terms of elementary functions of many thermodynamic relations.

CAMBRIDGE, MASSACHUSETTS

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

THE FORMATION OF OZONE IN THE ELECTRICAL DISCHARGE AT PRESSURES BELOW THREE MILLIMETERS[1]

BY JAMES K. HUNT

RECEIVED MAY 17, 1928 PUBLISHED JANUARY 8, 1929

Ozone formation in the electrical discharge has been studied chiefly at atmospheric pressures under conditions which give a non-uniform distribution of ionization. The purpose of this investigation was the study of the factors involved in the formation of ozone in an electrical discharge at low pressures, under conditions of somewhat greater uniformity. Pressures below three millimeters of mercury were employed and a high precision in the chemical analysis was demanded for these minute quantities of ozone.

In a previous communication from this Laboratory[2] the influence of the electrodes was studied down to 14 mm. and the ratio of electrode area to

---

[1] This *communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1926, under the direction of Farrington Daniels.*

[2] Newsome, THIS JOURNAL, **48**, **2035** (1926).

the volume of the discharge was made large. In the present research this ratio was made as small as possible in order to minimize the influence of the electrodes.

In one other research using a Siemens ozonizer and alternating current,[3] the pressure range has been carried down to 27 mm.

Apparatus and Procedure

The apparatus is shown in Fig. 1. The electrodes E, E' of the discharge tube T were connected to a source of high potential, S. An adjustable alcohol-xylene rheostat, R, of high resistance, was used for stabilizing and regulating the current. The induction coil, C, served to initiate the discharge, and the air gaps B, B' in the circuit prevented the short circuiting of the battery through the secondary of the coil. The potential drop across the tube was indicated by a Braun electrostatic voltmeter, V.

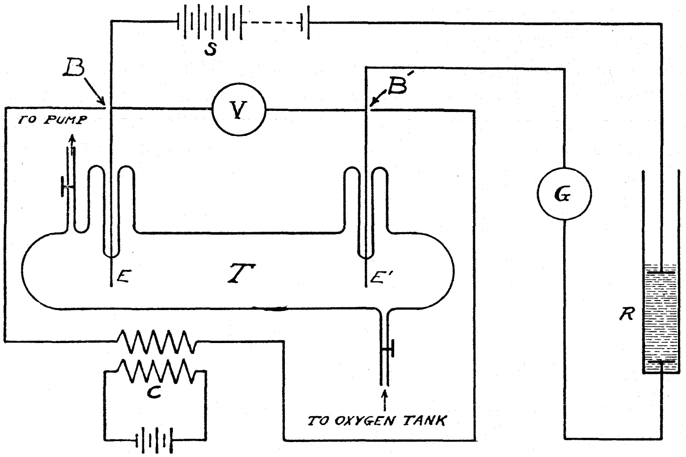


Fig. 1.—Discharge chamber and electrical connections.

The discharge tube was of soft glass about **60** cm. long and **7.2** cm. in diameter, with electrodes **45** cm. apart. These tubes had all-glass seals, but later another tube was used in which the electrode holders were sealed in with wax at a ground-glass joint to facilitate the interchange of different kinds of electrodes and to permit variation of the electrode distance.

Pressures within the discharge tube were read with a modified McLeod gage capable of measuring quickly and accurately from **3** mm. to **0.01** mm. of mercury. A Hyvac oil pump was used for evacuating the discharge tube down to **0.001** mm. The voltage for maintaining the discharge was obtained from 36 B batteries,[4] in series, giving a total potential of over 1600 volts. The current through the tube was measured with a shunted galvanometer which was calibrated to **0.05** milliampere. The electrodes of platinum, gold, aluminum and carbon were **0.4, 0.4, 1** and **2** mm. in diameter, respectively, and each was **3** cm. long. The electrodes of platinum foil were **1** cm. wide and **3.5** cm. long.

The whole tube was filled with a uniform blue glow during the discharge but the

---

[3] Warburg and Rump, *Z. Physik*, **32,245 (1925).**

[4] These batteries were kindly donated by the French Battery Co., Madison, Wis.

light was much more intense and somewhat lavender in shade around the electrodes, particularly around the negative electrode. The region of intense glow appeared to extend out about a millimeter from the electrodes under most of the conditions.

Carefully purified oxygen was used in the earlier experiments but subsequent experiments showed that the traces of hydrogen present in the electrolytic oxygen from a tank had no appreciable effect on the yield of ozone under the conditions of these experiments.

Preparatory to making a determination the tube was alternately exhausted and filled with oxygen several times to remove the nitrogen remaining in the tube. At a pressure of oxygen of about **2** mm. a current of **4** milliamperes was passed through the tube for five minutes to "age" the electrodes.

"Aging" was necessary since preliminary experiments had shown that with fresh electrodes the results were discordant and somewhat lower. This aging phenomenon was also observed by Anderegg[6] and Newsome.[2] After the preliminary discharge, the tube was twice evacuated and filled with oxygen to remove the ozone produced in the aging process. No ozone remained absorbed on the walls or electrodes after this treatment, as shown by the potassium iodide test.

After filling again with oxygen and evacuating to the desired pressure, the discharge was passed through the tube for a definite period of time while the current was carefully controlled and the voltage recorded. The tube was then disconnected and into it was carefully admitted about **80** cc. of **2%** potassium iodide solution. After shaking intermittently for half an hour the solution was run out, acidified with dilute sulfuric acid and titrated with $M/1000$ sodium thiosulfate solution, **1** cc. of which is equivalent to **0.000024** g., or **3.03** $\times$ 10^{17} molecules of ozone. Freshly prepared starch was used as an indicator and the titrations were carried out in **100-cc.** Nessler tubes. The end-point was accurate to about **0.1** cc. of thiosulfate solution.

Experimental Results

The variables of time, pressure, current, electrode area, electrode distance and electrode material were studied and the results are summarized[6] in Figs. 2, 3 and 4 and in Tables I, II and III.

The points in Figs. 2, 3 and 4 indicate the agreement to be expected. In general the yields of ozone increase slightly with successive check experiments.

TABLE I

VARIATION IN YIELD OF OZONE WITH DISTANCE BETWEEN ELECTRODES

Pressure, **1.9** mm.; current, **2** milliamperes; time, **30** seconds; platinum wire electrodes.

Dist. bet. elect.. cm.	Potential drop, volts	Molecules of ozone $\times 10^{-16}$	G. of ozone per k. w. hour	Dist. bet., elect.. cm.	Potential drop, volts	Molecules of ozone, $\times 10^{-16}$	G. of ozone per k. w. hour
6.5	560	18.5	1.6	37.5	875	29.8	1.6
6.5	560	19.7	1.7	37.5	875	31.9	1.7
6.5	560	22.8	1.9	45.0	1035	26.4	1.2
6.5	560	21.6	1.8	45.0	1035	36.4	1.7
24.0	760	23.7	1.5	45.0	1035	31.3	1.4
24.0	760	22.2	1.4				

---

[5] Anderegg, THIS JOURNAL, **39,2581 (1917).**

[6] Complete details are recorded in the thesis filed in the Library of the University of Wisconsin.

TABLE II

VARIATION IN YIELD OF OZONE WITH ELECTRODE AREA

Pressure, **1.9** mm.; platinum electrodes; current, **2** milliamperes; average results.

Cathode	Anode	Dist. bet. elect., cm.	Potential drop, volts	G. of ozone $\times 10^6$
Smooth wire	Smooth wire	24	760	18.1
Etched wire	Etched wire	24	700	17.8
Foil	Foil	24	600	23.6
Smooth wire	Smooth wire	37.5	875	24.3
Smooth wire	Foil	37.5	825	26.9
Foil	Smooth wire	37.5	750	46.2
Smooth wire	Point (wire broken off)	45	1250	28.8

TABLE III

VARIATION IN YIELD OF OZONE WITH ELECTRODE MATERIAL

Pressure, **1.9 mm.;** time, **30 seconds;** current, **2** milliamperes; distance between electrodes, 24 cm.

Electrode material	Potential drop, volts	G. of ozone $\times 10^6$	Electrode material	Potential drop, volts	G. of ozone $\times 10^6$
Platinum	760	18.7	Carbon	725	16.6
Platinum	760	17.5	Aluminum	600	24.2
Gold	760	19.2	Aluminum	600	69.2
Gold	760	18.5	Aluminum	600	84.5
Carbon	725	18.0	Aluminum	600	91.2

Interpretation of Experimental Results

Time.—In a closed tube the yield of ozone does not increase directly with the duration of the discharge, since an equilibrium is soon reached

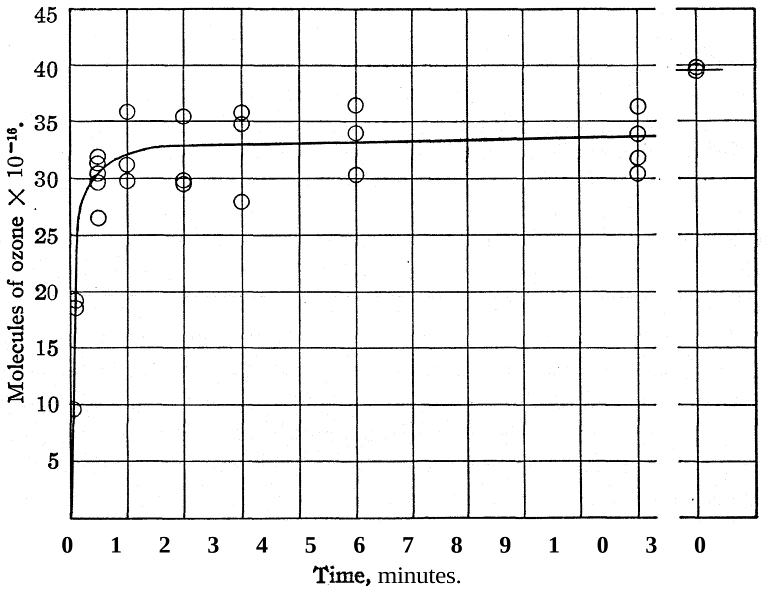


Fig. 2.—Variation in ozone yield with time. Pressure, **1.9** mm.; current, **2** milliamperes; potential drop, **850** volts; electrodes of platinum wire.

and the ozone is decomposed as fast as it is formed. The yields approach a limiting value, as shown in Fig. 2, and the yields per faraday and per kilowatt hour decrease with longer periods of time. During the first thirty seconds, however, the quantity of ozone is approximately proportional to the input of electricity, that is to the time, because the equilibrium mixture has not been reached and the concentration of ozone is so low that its decomposition is less important.

Pressure.—In Fig. **3** it is seen that the yield of ozone is greater at the higher pressures, perhaps on account of the greater number of collisions. Since the yield is limited by equilibrium conditions, it is not to be expected that the yield of ozone will vary directly with the pressure.

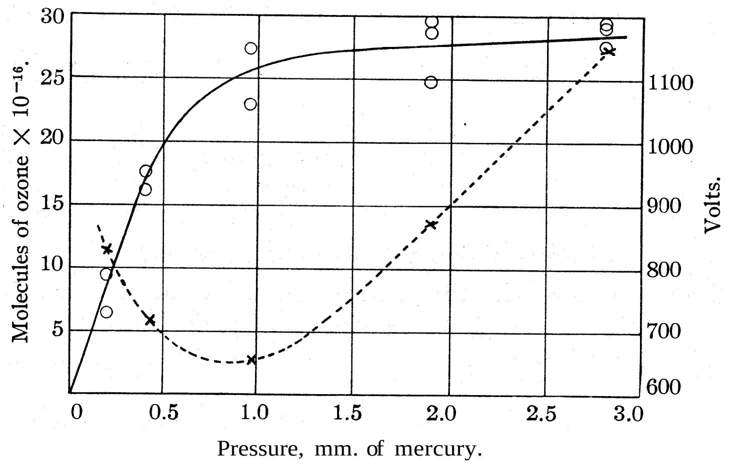


Fig. 3.—Full line: variation in ozone yield with pressure; broken line: variation in voltage with pressure at constant current; time, 30 seconds; current, 1 milliampere; electrodes of platinum wire.

Current.—Since the formation of ozone depends on the formation of ions, the yield must depend on the electrical energy input rather than on the current, for the current and the time constitute only the capacity factor of the electrical energy. Fig. 4 shows that as much ozone is formed with 1 milliampere as with 6 milliamperes. These facts indicate that the energy of which 1 milliampere is the capacity factor is sufficient to bring about in thirty seconds a state of approximate equilibrium and therefore it is not to be expected that more current (or energy) will result in a greater ozone yield.

Electrode Distance.—The full effect of increasing the distance between the electrodes is quite complicated but the chief factor is probably the greater energy input caused by the greater potential drop across the tube required to maintain a constant current. In Table I it is interesting to note that as the electrode distance increases the ozone yield increases, but the yield per kilowatt hour remains practically constant.

Electrode Area.—Table II shows that in most cases the yield of ozone is independent of anode area but somewhat dependent on cathode area. It is known that the potential drop is greatest at the cathode and that the ionization in the region around the cathode is much more intense than the ionization at the anode. Rideal and Kunz[7] found more ozone around the cathode than around the anode. An increase in the area of the cathode gives an increase in the volume of the cathode glow and increases the yield of ozone. The two experiments in which foil was used as the cathode are similar to those of Newsome[2] and suggest that in these two cases ozone may be decomposed at the anode.

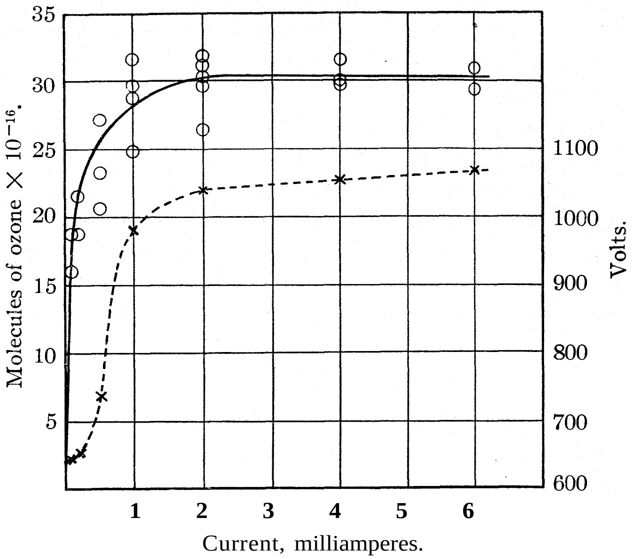


Fig. 4.—Full line: variation in ozone yield with current; broken line: variation in voltage with current at constant pressure; pressure, 1.9 mm.; time, **30** seconds; electrodes of platinum wire.

In the case of the etched electrodes, the volume of the cathode glow was the same as with the smooth electrodes and the yield of ozone was the same. The surface of the etched electrodes must have been greater than the surface of the smooth electrodes, but since the yield of ozone was no greater it may be concluded that the formation of ozone in these experiments was not strictly a surface phenomenon.

Electrode Material.—The data of Table III indicate that, with the exception of aluminum, the yield of ozone is independent of the electrode

---

[7] Rideal and Kunz, J. Phys. *Chem.*, **24**, **379** (1920).

material. This fact supports the view that under the conditions of the experiment, with small electrodes and low pressures, the formation of ozone occurs chiefly through the formation of gaseous ions in the discharge, probably in the vicinity of the cathode. In the work of Newsome[2] the conditions were different and the large electrodes led to the decomposition of the ozone at the surface after its formation.

An examination of the experimental data suggests that the influence of the electrodes was not completely eliminated in the present investigation, for a preliminary aging was found necessary, and even after the aging process there was an unmistakable tendency for each successive experiment of a series to give a slightly greater yield. The effect was so small, however, as to be nearly negligible in all cases except in that of the aluminum electrodes.

The results with aluminum electrodes are interesting. In the present investigation with small aluminum electrodes the ozone yield was high, while in the work of Newsome[2] with large aluminum electrodes and small current density the yields were very low. These two researches taken together appear to furnish a good example of the catalytic behavior of an electrode, giving an abnormally high yield when the ionization around the electrode is great and abnormally low yield when the ionization is small.

Theoretical Discussion

Before consideration of a possible mechanism of ozone formation it is necessary to make a calculation concerning the number of ions which is theoretically possible.

Taking the maximum potential necessary for the complete dissociation and ionization of oxygen as 23 volts,[8] it is easily calculated that 3.7×10^{-11} erg is required to form a pair of atomic ions in oxygen. The largest yield of ozone obtained in this investigation is the one corresponding to a current of 0.1 milliampere in Fig. 4, in which the time was thirty seconds, the potential drop 640 volts and the number of molecules of ozone produced 16.1 and 18.8×10^{16}. The energy input was 1.9 joules, giving an average yield of 26 g. of ozone per kilowatt hour. If all the energy of the discharge was used in making monatomic oxygen ions, it would be possible to produce during this thirty-second period 5.2×10^{17} pairs of ions ($1.9 \times 10^{7} \div 3.7 \times 10^{-11} = 5.2 \times 10^{17}$). Since 1.8×10^{17} molecules of ozone was obtained, the ratio of molecules of ozone to calculated ion pairs is 1/23.

It must be emphasized that this ratio gives only the order of magnitude, for it is assumed that all the ions require the maximum energy of 23 volts for their formation and that there is no decomposition of ozone. These

---

[8] **(a)** Smyth, *Proc. Roy. Soc.*, **105,** 116 (1924); (b) Franck and Jordan in "Anregung von Quantenspriingen durch Stösse," J. Springer, Berlin, 1926, p. 275, give 20 ± 1 volt.

assumptions are valid only as first approximations. The ionization potential for molecular oxygen is 15 volts instead of 23 volts, and the resonance potential is about 8 volts. As a matter of fact oxygen can be converted into ozone by ultra-violet light, which corresponds to this resonance potential (158 mμ) but other evidence indicates that the ionic reactions are more important in the electrical discharge. If 8 volts is taken as the energy necessary for ozone formation instead of 23 volts, the number of ozone molecules formed for a given energy input is three times as great and if 15 volts is taken, the ratio of molecules of ozone to calculated number of ion pairs becomes 1/3.6 instead of 1/2.8.

There is considerable decomposition of ozone even at the low concentrations, and a rough extrapolation of the yield per kilowatt hour to zero current indicates a yield about three times as large as the largest yield obtained in these experiments, namely, 3 × 26 g. per kilowatt hour. This extrapolation suggests an M/N ratio of approximately 1, if an ionization potential is used for the calculation, but the extrapolation is too inaccurate and the uncertainties of analysis for the short experiments are too great to draw any conclusions.

The discharge tube contained 2.3 liters of oxygen at 1.9 millimeters' pressure, or about 1.5×10^{20} molecules of oxygen. The number of pairs of ions produced in thirty seconds was about 5.2×10^{17}, or a ratio of about 150 molecules to 1 ion if the ions retained their charges as long as 30 seconds. Actually the ratio of the concentration of molecules to the concentration of ions was much greater than this, because the ions were discharged very rapidly.

The large excess of molecules over ions demands a predominating mechanism which involves reactions between ions and molecules, rather than between ions and ions. It must be borne in mind, however, that although the collisions between ions and molecules predominate greatly the collisions between positive and negative ions are not entirely fortuitous, since a force of attraction tends to draw them together.

The following reactions are offered as giving a possible mechanism for ozone formation in the electrical discharge. Several other intermediate steps also may be involved.

$$O_2 = O^+ + O^-$$

$$O^+ + O_2 = O_3^+ \text{ and } O^- + O_2 = O_3^-$$

$$O_3^+ + O_3^- = 2O_3 \text{ or } O_3^+ + O^- = 2O_2 \text{ and } O_3^- + O^+ = 2O_2$$

According to these reactions, one molecule of ozone should be produced by each pair of ions and this M/N ratio of 1 is not incompatible with the experimental results of this investigation.

Other mechanisms are possible such, for example, as the formation of an ion cluster surrounding an ionized molecule (instead of an ionized atom), but at least three oxygen molecules are required for each cluster in order that it may break up into O_3 molecules, and the mass spectrograph data so far available show a high concentration of charged atoms of oxygen and very low concentration of O_6 ions.

The author desires to express his appreciation to Professor Farrington Daniels for his guidance throughout this investigation and to E. I. du Pont de Nemours and Company for the fellowship held during a portion of the time this work was in progress.

Summary

1. The formation of ozone in the glow discharge has been investigated in a closed tube at pressures from 0.2 to 2.8 mm. The ozone was determined by chemical analysis.

2. The electrodes were small, minimizing any catalytic effect.

3. The effect of the following variables on the ozone yield has been studied: *(a)* duration of discharge, (b) pressure, (c) current, (d) distance between electrodes, *(e)* area of electrodes, *(f)* material of electrodes.

4. An equilibrium concentration of ozone was reached in less than a minute.

5. The yield of ozone increased with increasing pressure, but at a decreasing rate.

6. The yield of ozone increased with increasing cathode area.

7. The yield of ozone was independent of electrode material, except that aluminum gave abnormally high results.

8. The highest yield obtained was 26 g. per kilowatt hour, but all yields were low on account of the decomposition of ozone.

9. A calculation on the basis of ionization potentials indicates that the number of pairs of ions and the number of molecules of ozone produced are both of the same order of magnitude.

10. The predominating mechanism of ozone formation is possibly one involving collision between monatomic oxygen ions and neutral molecules.

MADISON, WISCONSIN

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

THE ELECTROMETRIC TITRATION OF MANGANESE BY THE VOLHARD METHOD[1]

BY B. F. BRANN AND M. H. CLAPP

RECEIVED JUNE 25, 1928 PUBLISHED JANUARY 8, 1929

The Volhard method is generally recognized as one of the best of the volumetric methods for the determination of considerable amounts of manganese, the chief objection to its use being the difficulty in recognizing the end-point in the presence of the heavy brown precipitate which forms during the titration. An electrometric method of determining the end-point would seem, therefore, to be particularly desirable in this case.

Several attempts have been made in this Laboratory[2] to apply the electrometric method to this titration, using the ordinary potentiometer system with calomel–platinum electrodes and also using the polarized electrode system described by Willard and Fenwick.[3] Neither of these methods gave satisfactory results. A break was obtained near the end-point but it was uncertain and irregular. Miiller and Wähle,[4] using the ordinary potentiometer system, state that about seven minutes is required to attain constant potential when near the end-point. The method of differential titration described by Cox[5] and modified by MacInnes and Jones——as also tried but without satisfactory results, due probably to the slowness with which constant potential is attained. Finally, the method described by Foulk and Bawden,[7] and called by them the "dead stop end-point" was tried and, after some modification, was found to give satisfactory results.

Discussion

In the dead stop end-point as described by Foulk and Bawden, two platinum electrodes were used in the solution to be titrated and a very small potential was applied to the electrodes, a potential so small that the back electromotive force of polarization balanced it and no current flowed, as shown by the zero deflection of a galvanometer in the circuit. At the end-point of the titration both electrodes were depolarized and a permanent galvanometer deflection was obtained. Assuming the polarization to be due to oxygen at the anode and hydrogen at the cathode, it is evident that in order to obtain a permanent galvanometer deflection the

---

[1] A considerable part of the preliminary work on this method was done by M. H. Clapp as a part of his Senior Thesis, 1927.

[2] Senior Theses by A. M. Varney, 1921, and E. E. Lineken, 1923.

[3] Willard and Fenwick, THIS JOURNAL, 44,2504 (1922).

[4] Muller and Wahle, *Z. anorg. allgem. Chem.*, **129**, 33 (1923).

[5] Cox, THIS JOURNAL, 47,2138 (1925).

[6] MacInnes and Jones, *ibid.*, 48,2831 (1926).

[7] Foulk and Bawden, *ibid.*, 48, 2045 (1926).

anode must be depolarized by some suitable reducing agent and the cathode by some suitable oxidizing agent.

Now in the Volhard titration of manganese, a practically neutral solution of a manganous salt is being titrated with permanganate and accordingly the cathode will become depolarized as soon as a slight excess of permanganate has been added to the solution. No satisfactory means of depolarizing a platinum anode in this solution could be devised, but if the platinum is replaced by silver and a trace of chloride ion is added to the solution, a permanently depolarized anode is obtained and the flow of current through the solution and consequent galvanometer deflection is controlled wholly by the polarization or depolarization of the cathode. Furthermore, when a silver anode is substituted for platinum, a potential is developed between the two electrodes and no outside source of current is required.

Experimental Method

The apparatus required is very simple; the titrations may be made in a 400-cc. beaker, a short piece of platinum wire being used as the cathode and a piece of silver wire as the anode. The electrodes are connected directly to a galvanometer. A good mechanical stirring device is also essential and it is desirable to have the apparatus so arranged that the beaker may be heated during titration either by a small hot-plate or directly by a burner.

The solutions are prepared for titration in the usual way with the addition of 2 or 3 drops of 6 *N* hydrochloric acid to furnish the necessary chloride ion. As the permanganate is added the galvanometer needle fluctuates violently but no permanent deflection is obtained and if the addition of permanganate is stopped for a short time the needle returns slowly to zero. As the end-point is approached, the needle returns more and more slowly toward zero, and at the end-point a full scale deflection is obtained which remains unchanged for a considerable time.

The temporary depolarization of the cathode before the end-point is reached may be due in part to deposition on the cathode of finely divided zinc manganite, which acts as a depolarizer and produces a galvanometer deflection which may be mistaken for the true end-point unless the titration is conducted with due care. The last few drops of permanganate should be added one at a time, waiting after each drop until the galvanometer needle begins to return toward the zero point. The final drop produces a full scale deflection which persists for a considerable time, the exact time depending on the sensitiveness of the galvanometer and the surface area of the cathode. In case of doubt, the end-point may be checked by filtering a little of the solution and noting the color. With the proper combination of galvanometer and electrodes, a definite electrometric end-point may be obtained with a very slight excess of permanganate, giving an almost imperceptible pink color to the solution.

The following table shows the results actually obtained in two series of nine consecutive titrations. The test solutions were made by reducing approximately 0.1 N permanganate with hydrogen peroxide in sulfuric acid solution. Three drops of 6 *N* hydrochloric acid were then added and the solution was made just neutral to methyl orange with ammonia. Five grams of zinc sulfate was added, the solution was diluted to about 300 cc., heated to 90° and titrated as previously described with the approximately 0.1 N permanganate. The first column of the table shows the volume of permanganate reduced; the second column gives the theoretical volume of permanganate required for titration, which is two-thirds of the volume reduced plus a 0.05 cc. blank for the zinc sulfate used; the third and fourth columns give the volume of permanganate actually used and the titration error.

TABLE I

RESULTS OF TITRATIONS

$KMnO_4$ reduced, cc.	$KMnO_4$ required, cc. Theoretical	Actual	Error	$KMnO_4$ reduced, cc.	$KMnO_4$ required, cc. Theoretical	Actual	Error
16.37	10.97	11.03	+0.06	18.10	12.11	12.11	0.00
16.97	11.37	11.39	+ .02	18.24	12.21	12.25	+ .04
16.05	10.75	10.83	+ .08	18.20	12.19	12.19	.00
25.48	17.03	17.03	.00	28.42	18.99	18.98	− .01
26.29	17.57	17.57	.00	28.02	18.73	18.68	− .05
28.03	18.68	18.71	+ .03	28.52	19.07	19.03	− .04
32.07	21.43	21.40	− .03	47.77	31.89	31.86	− .03
32.48	21.71	21.71	.00	42.59	28.45	28.40	− .03
34.78	23.18	23.22	+ .04	36.08	24.11	24.08	− .03

The galvanometer used in most of this work was a pointer type instrument with a rated sensitivity of one scale division per microampere and a resistance of 250 ohms. With this galvanometer connected directly to the electrodes, and using 3 cm. of platinum wire (about 0.05 cm. in diameter) as a cathode, the end-point was shown by a full scale deflection which remained unchanged for a full minute. With a galvanometer of twice this sensitivity and 1000 ohms' resistance, about a minute and a half had to be allowed at the end-point when the same electrodes were used. With a given galvanometer, the time required for the end-point probably can be regulated to a considerable extent by varying the area of the cathode.

The size and nature of the silver anode seem to be immaterial. Ordinary silver wire was used most of the time, but both platinum wire and platinum foil plated with silver were used also with no apparent difference in result. The silver plate, however, is gradually converted into silver chloride and requires occasional renewal.

It seems to be necessary to clean the electrodes frequently, possibly after each titration. The adhering zinc manganite may be removed easily by dipping the electrodes in acidified hydrogen peroxide solution and the film of silver chloride can be dissolved from the anode with ammonia.

Summary

A modification of the "dead stop end-point" method of electrometric titration has been described, and it has been shown that this method may be applied satisfactorily in the Volhard titration of manganese.

ORONO, MAINE

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

STUDIES ON THE HIGHER OXIDES OF SOME RARE-EARTH ELEMENTS[1]

BY H. ARMIN PAGEL AND PAUL H. M.-P. BRINTON

RECEIVED JUNE 27, 1928 PUBLISHED JANUARY 8, 1929

Introduction

The sesquioxide, R_2O_3, may be assumed as the type of the normal oxides of the rare-earth elements; on that all are agreed, but the literature dealing with oxides of types higher than R_2O_3 is full of uncertainty and contradictions. Yet in the placing of these elements in the periodic table we find many assumptions of higher oxides, the existence of which has never been proved, and without this proof there seems little justification for placing several of the rare-earth elements in the columns with quadri- and quinquivalent elements. Of the oxides of the true rare earths those of praseodymium have been investigated most frequently, but with very uncertain results. The oxide resulting from the ignition of praseodymium compounds in air, formerly considered as Pr_4O_7, has been shown[2] to conform more nearly to the formula Pr_6O_{11}. Another oxide, PrO_2, has been prepared, although never quite pure, and divergent opinions have been expressed as to the methods of its formation and the conditions for its stability. Brauner[3] claimed to have prepared the dioxide by heating a mixture of praseodymium and potassium nitrates at 400°. He also reported[4] the preparation of Pr_5O_9, Pr_2O_5, Nd_2O_4 and Nd_2O_5, but failed to give details for their preparation. Marc[5] concluded that the presence of a little cerium is necessary for the higher oxidation of praseodymium, and that under these conditions neodymium is also oxidized. These results, as well as those of Meyer and Koss,[6] were obtained with mixtures, the relative proportions of which were arrived at indirectly, and the results cannot be regarded as entirely conclusive, as Meyer[7] admits in a later paper. Von Scheele[8] reported the preparation of the dioxide by heating praseodymium oxalate in air to incipient redness. His analyses showed from 4.09 to 4.97% "excess oxygen" "(that is, over that demanded by the

---

[1] From a thesis submitted to the Graduate Faculty of the University of Minnesota by H. Armin Pagel in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Schottlander, *Ber.*, 25,569 (1892); *(b)*Meyer, Z. *anorg. Chem.*, **41,** 97 (1904); *(c)* Brinton and Pagel, THIS JOURNAL, 45, 1460 (1923); (d) Prandtl and Huttner, *Z. anorg. allgem. Chem.*, 149,235 (1925).

[3] Brauner, *Proc. Chem. Soc.*, 14, 70 (1898); 17, 66 (1901).

[4] Brauner, *Z. anorg. Chem.*, 32, 1 (1902).

[5] Marc, Ber., 35, 2370 (1902).

[6] Meyer and Koss, *ibid.*, 35,3740 (1902).

[7] Meyer, *Z. anorg. Chem.*, 41, 97 (1904).

[8] Von Scheele, *ibid.*, 17, 310 (1898).

formula Pr_2O_3)." The calculated "excess oxygen" for PrO_2 is 4.64%, so his "yields" were approximately from 88 to 107%. Meyer[7] obtained a dioxide of about 97.5% purity by heating praseodymium nitrate with potassium nitrate at 440–450°, as recommended by Brauner. Prandtl and Huttner,[2d] attempting to duplicate the experiments of Meyer and Brauner, found a product corresponding to the formula $Pr_6O_{11}\cdot 7H_2O$ instead of PrO_2. Their purest dioxide was obtained by heating the sesquioxide for five days in an atmosphere of oxygen at about 300". Neodymium was found to form no higher oxides when fused with sodium chlorate. Other investigations will be reviewed later in connection with our own conclusions.

In this paper we present the results of studies on the preparation and stability ranges of the oxides of lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium and ytterbium. It is hoped that oxides of other rare-earth elements, especially terbium, will be treated in a later paper.

Materials and Apparatus

The lanthanum, praseodymium, neodymium, samarium and gadolinium compounds were those described in a previous communication,[9] and further discussion of their high purity is not necessary. Before final precipitation as oxalates finely divided ashless filter pulp was added to the solutions in order to impart the desired fineness and porosity to the ignited oxides. Otherwise the oxides are so coarse and dense that reduction by hydrogen is very slow, and possibly not entirely complete.

The erbium and ytterbium compounds were purchased in the market. Special investigation of their purity was deferred, pending evidence of positive results in the formation of higher oxides.

For pressure oxidations tank oxygen of 99.5% purity was employed, after passage through a drying train. The use of hydrogen generated in the Laboratory was soon abandoned in favor of commercial electrolytic hydrogen, since after passage through the purification train the gas from the two sources gave identical results. The train consisted of (1) acid permanganate solution, (2) alkaline permanganate solution, *(3)* heated copper spirals in a copper tube, (4) moistened silver nitrate crystals, (5) potassium hydroxide solution, (6) concentrated sulfuric acid and (7) a tower of phosphorus pentoxide.

Balance.—It soon became evident that errors due to absorption of moisture and carbon dioxide by some of the very hygroscopic rare-earth oxides were quite appreciable, when dealing with small changes in weight, so a special balance was arranged to eliminate this source of error. A Christian Becker No. 8A chainomatic balance, having a graduated notched beam which allowed weights up to 1.1 g. to be adjusted without opening the door, was found entirely reliable as to constancy. The beam and chain

---

[9] Sarver and Brinton, THIS JOURNAL, 49,943 (1927).

readings were accurately calibrated. The balance case was dismantled, all woodwork was varnished, and all cracks were filled with melted paraffin. The hole through the base accommodating the pan-arrest bar was covered with a thin rubber membrane (a dental rubber dam), which was sealed to the bar and base with adhesive tape. The front door was permanently sealed with tape and paraffin. Under the back door, which was raised about 10 cm., was sealed a board containing a brass tube, C, Fig. 1, of very slightly larger bore than the Pyrex tube, **A.** This tube was located directly behind the left pan of the balance. **A** nail driven into a wooden block, F, serves as a bumper to prevent disalignment of the pan when the boat is pushed onto it from the tube. B represents a wooden frame in which operates a snugly fitting metal slide-gate, D, which serves to seal the entrance when the Pyrex tube is not in place. **A** velvet lining, E, gives an almost air-tight joint between the wood and the glass tube. Behind the right pan a hole, ordinarily closed with a 1-hole stopper, allows the integral weights to be handled with a wire fork. **A** gentle stream of purified air passed through this stopper into the balance case at all times except when weighing. Thus it was never necessary to open the balance door except to change the desiccating and decarbonating reagents kept in the case. The technique of weighing will be described later.

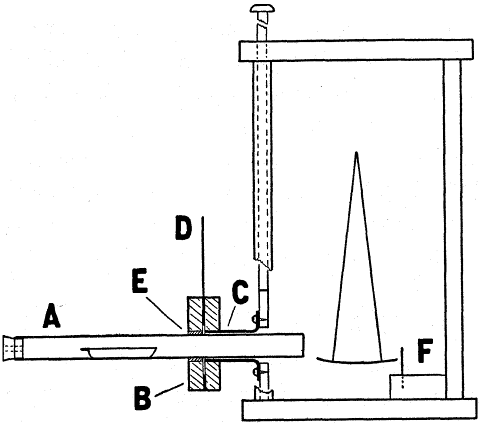


Fig. 1.—Side view of balance.

Pressure Furnace.—While a rebuilt Hoskins furnace with projecting core served for air ignitions and hydrogen reductions, a special furnace had to be built for the oxidations by oxygen under high pressures.[10] The furnace is diagrammatically shown in Fig. 2. **A** is the outer shell, 46 cm. long, of triple strength wrought iron, 8 mm. thick. The dotted lines just inside this shell, and at the ends, represent heavy wire screening, to facilitate the rapid distribution of oxygen when building up the pressure.

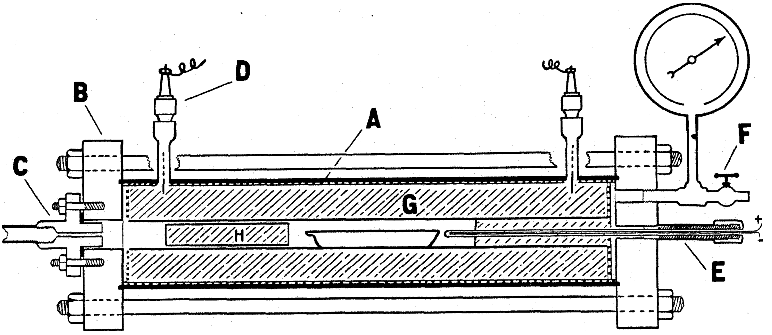


Fig. 2.—Pressure oxidation furnace.

---

[10] After the completion of this work a somewhat similar type of furnace was found described by Fischer and Ploetze, *Z. anorg. Chem.*, **75**, 1 (1912).

The ends, B, are solid cast iron caps, 17.8 by 3.8 cm., grooved to take copper gaskets, and they were drawn against the accurately machined ends of the shell, A, by eight iron bolts, only two of which are shown in the cut. This gave a perfectly tight joint. C is a flanged bronze coupling, secured by four bolts, with copper–asbestos gaskets to prevent leakage. This coupling leads to the oxygen supply and provides an entrance to the silica tube, which is wound with 22-gage Chromel wire. To prevent too high a temperature at the junction points, 15 cm. of heavy Chromel wire was welded to each end of the heating wire. Eight-cm. lengths of regular $^3/_8$ inch iron pipe coupling were fitted into the jacket about 8 cm. from each end, and to these couplings Champion spark-plugs, D, were fitted by means of reducers, the joints being made air-tight with "Caulk" dental cement. Litharge-glycerin cement proved less satisfactory for joints which could not be water cooled, as there was a slight decomposition of organic matter at high temperatures. The terminals of the heating elements, insulated with Pyrex tubing, were attached to the spark-plugs with small hollow brass cylinders, slotted on each end, driven on the protruding end of the electrodes. After screwing the body of the plug into the reducer, the core of the plug was introduced, slipping the slot onto the terminal wire. This gave a very satisfactory contact. E shows a quartz thermocouple tube sealed into an iron nipple, fitted with a brass cap. This was made tight with lithare-glycerin cement and was water-cooled. The brass needle valve, F, was used for evacuating the furnace The pressure gage was calibrated at the Air Reduction Plant, in Minneapolis, by comparison with their standard test gages. The annular space between the furnace wall and the combustion tube was packed with ignited asbestos wool, *G*, as was also the end of the combustion tube into which the thermocouple extended. To prevent radiation toward the other end of the heating chamber an Alundum tube. H, loosely packed with asbestos fiber, was inserted. Acknowledgment is gratefully made to Mr. F. W. Fullerton, Mechanician of the School of Chemistry of the University of Minnesota, and to Mr. Frank L. Heyer, Jr., of Dakota, Minnesota, for valued assistance in the construction of this furnace.

The temperature gradient was determined by means of two thermocouples. One was in its permanent position, as shown in the cut, while the other was moved, in 1 cm. stages, over the space occupied by the longest boat. These thermocouples were calibrated against one certified by the U. S. Bureau of Standards. Over the range tested a maximum variation of 7° was found, and except at the very ends of the longest boat the temperature range was not over 2° greater or less than the temperature found by adding 4° to the reading of the regular thermocouple. Therefore all temperatures recorded in this paper were obtained by adding 4° to the observed temperature. All temperatures were read with a potentiometer indicator.

Experimental Part

Composition of the Oxide of Praseodymium after Ignition in Air.— In a previous communication[2] it has been shown that the formula for praseodymium oxide obtained by ignition in air at ordinary pressures agrees very closely with Pr_6O_{11}. This oxide had been slowly cooled in the furnace before being transferred to a desiccator. Later experiments confirmed the correctness of this formula for the slowly cooled oxide, but a question arose as to the effect of varying the conditions of cooling. The following set of experiments was planned to throw light on this point.

3.4636 *g.* of purest praseodymium sesquioxide was employed. This had been prepared by igniting the oxalate in a large porcelain boat and then reducing with hydrogen at about 900" to constant weight. To guard against the possible presence of weighable amounts of sulfur, as basic sulfate, the sample was treated with steam and hydrogen, and again reduced in dry hydrogen. No change in weight was observed. In these hydrogen reductions the gas was allowed to pass during the cooling until a temperature of about 50" was reached, after which purified air was substituted for the hydrogen. While the purified air continued to flow, the Pyrex tube, A in Fig. 1, was attached to the combustion tube, and the boat was pulled into it. The tube was stoppered and carried to the balance. Purified air was again passed through the tube, the gate, D in Fig. 1, was raised and the tube was slipped into place. The air current was then disconnected from the tube A, and passed into the balance case through the hole back of the right pan. With the stopper in the back end of the tube now removed, the purified air passed in the reverse direction through this tube, and this enabled the boat to be pushed onto the balance pan without the introduction of any unpurified air. After shutting off the air and stoppering the Pyrex tube, a brief pause was allowed for subsiding of air currents, and the boat was then weighed. The same technique was used in all weighings of such oxides as showed a tendency to absorb moisture. Controls with samples of ignited calcium oxide, mixed with a little calcium chloride, proved this method ideally suited to the handling of hygroscopic and carbon dioxide susceptible substances.

In Table I are shown the results of several variables. It will be readily understood that with the furnace slightly tilted, both ends of the tube being open, a current of air would be induced during the cooling, so that conditions would be more favorable for re-oxidation. When the cooling conditions are spoken of as "rapid" in the table it means that the boat at its maximum temperature was pushed to the cool end of the tube outside the furnace. A great many experiments, carried out with smaller quantities of the oxides, gave results agreeing closely with those shown in the table. Tabulation of these runs is omitted for economy of space. In the interest of later discussion the results in this table are placed in the order of decreasing yields.

It will be seen that the slowly cooled runs give the highest values. Under conditions of rapid cooling in a level furnace we find the minimum values. In the last run of this series a hinged furnace was used, so the tube could be lifted from the heat, stoppered and cooled very rapidly in diminished oxygen pressure. It seems justifiable to conclude that the rate of cooling and the supply of oxygen during the cooling period are the main factors in determining the composition of the oxide.

That the oxide heated over long periods of time at relatively low temperatures gives oxygen ratios higher than Pr_6O_{11} was found in an attempt to determine roughly the rate of decomposition of the dioxide. **A** sample

TABLE I

RESULTS OF SEVERAL VARIABLES

Heating time	Temp, °C.	Cooling conditions	Tilt	Mole % of PrO_2[a]
20 min.	700	To 25° in pure air in furnace	Level	66.9
5	700	To 160° in furnace	7°	66.7
1 hr.	700–725	To 200° in furnace	7°	66.6
1.5	840–860	To 450° in furnace	Level	66.3
1	700–725	Rapid	7°	64.5
2	900–915	Rapid	7"	64 0
2	850	Rapid	7°	63.9
0.5	850	Rapid	7"	63.4
1	850–875	Rapid	3.5	63.4
1.5	900-925	Rapid	Level	61.0
15 min.	950	Tube stoppered and lifted from furnace		55.7

[a] CALCULATIONS.—In most papers dealing with the higher oxides of praseodymium the compositions have been indicated in terms of "excess oxygen." Thus PrO_2 contains 4.647, oxygen in excess over Pr_2O_3. This method is somewhat unsatisfactory because the percentages of "excess oxygen" in the higher oxides are so small that even a slight difference in this percentage actually represents a considerable difference in the composition, and concordance of analytical figures with "theory" gives one the impression of much greater purity than is actually the case. Much of the past work on these oxides, when viewed in the light of a 100% basis, is not convincing. It is for this reason that we have used the largest possible samples, and adopted the manipulative refinements described in this paper. In our tabulations and discussions results are expressed in terms of molecular percentages of praseodymium dioxide formed. For example 98 mole % of PrO_2 means that oxidation of the sesquioxide has occurred to such a degree that the empirical composition of the resulting oxide could be expressed by saying that for every 98 molecules of PrO_2 formed, 1 molecule of Pr_2O_3 remains unoxidized. Pr_6O_{11} would correspond to 66.67 mole 7, of PrO_2, and if the actual percentage purity of a sample in terms of molecules of Pr_6O_{11}, considered as a definite compound, is desired, it can be obtained by simply multiplying the mole % of PrO_2 by 1.5.

of about 93 mole % of PrO_2 heated for five hours in a current of pure air at 375° yielded a composition of 83.6%. Further heating for thirteen hours at 385–395° changed the composition to 70.7%. The heating was continued for periods of thirteen, twenty-one and twenty-two hours at the same temperature and in each of these determinations a constant value of 68.1% was found. Attempting to approach this constant value from the lower side, a sample of 64.5 mole % of PrO_2 was heated in a gentle air current at 385–395° for periods of seven, twenty-four and six hours, and compositions of 68.0, 68.4 and 68.4% were found. This sample was then heated in the open furnace, tilted at an angle of 7°, without forced air current, for twenty hours at 460–495°, and again for twenty hours at 480–510°, and identical values of 67.7% were obtained.

In the work on pressure oxidation to be described later it was frequently necessary to prepare samples of known weight of Pr_2O_3 by hydrogen reduction. The reduced oxide was then re-oxidized in air at 900–950°

for twenty minutes, in the tilted tube furnace and rapidly cooled. Consistent values of **64.1–64.3** mole % of PrO_2 were always obtained, and this regardless of whether we started with pure Pr_2O_3 or almost pure PrO_2.

Thus it is seen that the composition of the air-ignited oxide of praseodymium can be made to vary with the conditions of ignition and cooling—especially are the conditions of cooling important—but with any specified set of conditions reasonably concordant results are found.

Preparation of Praseodymium Dioxide by Pressure Oxidation.—From the evidence of work thus far done it was thought likely that a quantitative yield of praseodymium dioxide could be obtained by heating and cooling in an atmosphere of pure oxygen at very high pressure. Preliminary tests in the first pressure furnace constructed gave apparent yields of **100.6** to **100.7** mole % of PrO_2 by heating for twenty hours at 350° in pure oxygen at a pressure of **195** lb./sq. in. Fearing that the high values might be due to adsorption of oxygen during the cooling under high pressure, the furnace was thoroughly evacuated at high temperature, then filled with oxygen and cooled to room temperature. An oxide sample of constant weight was introduced, allowed to stand for five hours at a pressure of **215** lb. of oxygen and weighed. An increase of only **0.2** mg. was found. The excess in yield over **100%** was not large, but with the highly refined manipulations employed it could not be considered as allowable experimental error. Moreover, a slight odor had been noticed in the exhaust oxygen, and it was thought that the error might be due to absorption of volatile organic matter from the decomposition of the cement used. This led to the construction of the new furnace, substituting dental cement for the litharge-glycerin mixture. The work was started anew, and the pressure oxidation results obtained up to that time were discarded.

To determine the effects of the variables, time, temperature and pressure, series of runs were made in which two of the factors were held constant while the third was varied. Each pressure oxidation was followed by a quickly-cooled air ignition in the tilted furnace, which gave uniform

TABLE II

THE EFFECT OF TEMPERATURE

Pressure, 215 lb./sq. in. (±5 lb.). Time, 5.25 hours. Temp. control ±2°. 1.3394 g. of Pr_2O_3.

Temp., °C.	Mole % of PrO_2	Temp., °C.	Mole % of PrO_2	Temp., °C.	Mole % of PrO_2
205	64.9	306	76.2	405	98.7
204	64.9	306	77.1	405	98.7
230	67.0	329	84.5	430	80.2
230	66.6	329	86.5	430	81.7
255	68.6	350	97.8	453	76.6
255	68.2	352	97.2	451	76.9
278	70.9	384	98.0	509	76.6
278	70.4	386	97.8	585	74.6

compositions corresponding to 64.1–64.3 mole % of PrO_2. In all reports true pressures are given, that is, gage pressures plus 15 lb./sq. in. At the end of each series the sample was reduced in hydrogen and weighed as sesquioxide, to make certain that no manipulative loss had occurred.

The results in Table II are graphically shown in Fig. **3.** The sharp drop in yield beyond 405° suggests that at temperatures above that point the dissociation pressure of the dioxide exceeds 215 lb. The curve would undoubtedly drop to a minimum much lower than that shown at temperatures 440–585° if the true conditions existing during the entire run could be shown. It is impossible to cool the furnace instantaneously, and thus preserve the stage of oxidation which exists at any instant. It was found that from temperatures around 500° a nearly uniform rate of cooling of about 10° per minute held for the first twenty minutes. It seems reasonable to expect that a certain amount of re-oxidation occurs in passing through the temperature range most favorable to a high rate of oxidation, 400–325°. This point was, in fact, proved by introducing the air-ignited oxide (64.2 mole % of PrO_2) into the furnace at temperatures of 506, 504, 454 and 448°, letting in oxygen as rapidly as possible up to 215 lb. pressure, and then immediately shutting off the heating current. These four runs showed, respectively, 75.0, 75.5, 75.4 and 75.6%, values which lie only about 1% lower than those obtained in five and one-fourth hours at the same temperatures.

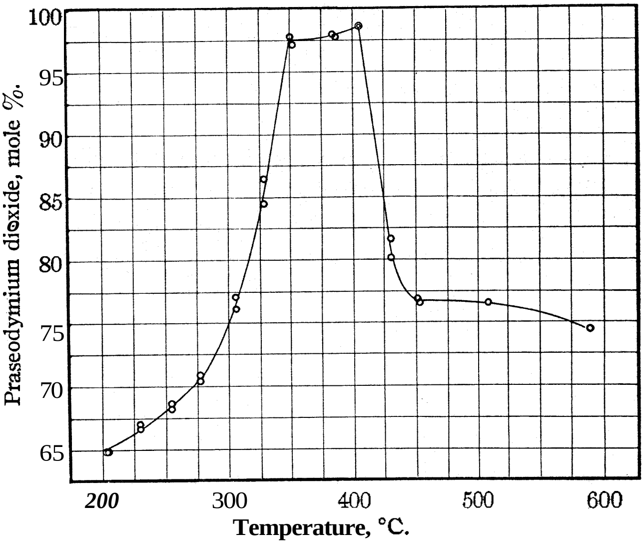


Fig. 3.—Effect of temperature on the formation of praseodymium dioxide; time of each heat, $5^1/_4$ hrs.; oxygen pressure, 215 lb./sq. in.

The effect of varying the time of heating, at the optimum temperature, and at three different pressures, is shown in Table III.

TABLE III

THE EFFECT OF TIME

Temp, 378 ± 3°

215 lb /sq. in.				115 lb /sq. in.		65 lb./sq. in.	
Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %	Heating, hours	PrO_2, mole %
0.75	77.4	3.75	97.1	0.75	71.0	1.5	67.9
0.75	77.2	5.25	98.0	1.5	73.2	3	68.6
1.5	85.8	5.25	98.0	2.25	76.7	4.5	68.0
1.5	85 8	8	99.1 (356°)	3	79.4	6	68.4
2 25	95.1	11.5	99.2 (370°)	5	95.7	13	68.9
2.25	94.3	12	99.1 (375°)	5	95.0		
3	96.3	15	99.2 (355")	10	97.0		
3	97.4						

The values in this table are shown graphically in Fig. 4, Curves A, B and C showing values for pressures of 65, 115 and 215 lb., respectively.

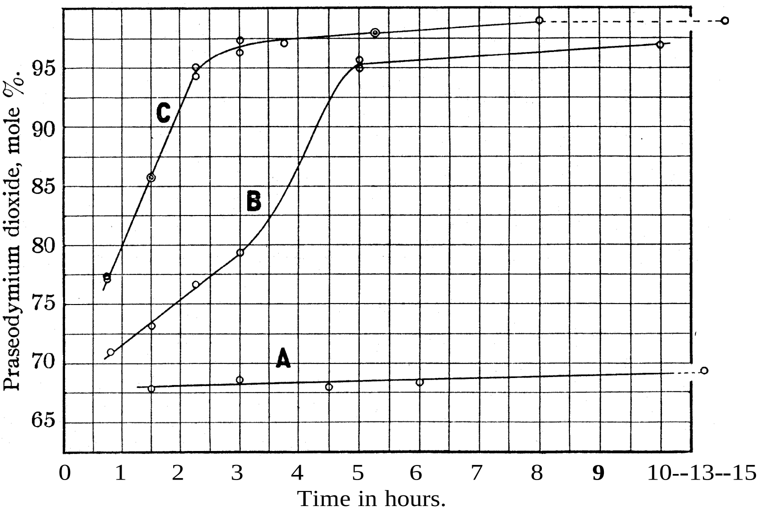


Fig. 4.—Effect of heating time on formation of praseodymium dioxide at pressures of A, 65 lb.; B, 115 lb.; and C, 215 lb. of O_2/sq. in.

It seemed impossible to increase the yield beyond 99.2% of PrO_2. (At figures near 100% the molecular percentage and the weight percentage are almost synonymous.) To be certain of the completeness of the hydrogen reductions upon which the calculations are based, four successive hydrogen reductions were made, and they showed splendid concordance. Then, after ignition in air, another hydrogen reduction of two hours' duration showed perfect agreement with the former values. It seems unreasonable, then, to question the completeness of the reduction. Nevertheless, if one wished to dispute this point, an argument could be made of the fact that the maximum oxidation shows as good concordance as the maximum reduction, and perhaps we have obtained pure dioxide, but never pure sesquioxide. This, however, is less likely.

In a final attempt to get a perfect yield, a larger sample of the sesquioxide (over 3.5 g.) was taken to minimize experimental errors and subjected to pressures up to 400 Ib., with temperatures varying from 345 to 405°, approaching this range from the higher as well as from the lower side. Increased pressure showed more rapid oxidation, 99.2% being obtained in three and five-tenths hours at 365 lb. and 353°, and 98% in thirty-five minutes at 390 Ib. and 400°, but the final result of continued heating could not be made to exceed 99.2% of praseodymium dioxide.

Effect of **Ceria** on the Formation of Higher Oxides of Praseodymium.—The catalytic effect of small amounts of ceria has been held responsible by some investigators for the contradictory results obtained in the study of the higher oxides of praseodymium.

A mixture of 98% praseodymium sesquioxide and 2% ceric oxide was prepared by precipitating as oxalate a nitrate solution containing 1.0637 g. of Pr_2O_3 and 0.0213 g. of CeO_2. Hydrogen reduction of the mixed oxides gave 1.0852 g. (calculated value, on the assumption that ceria is not reduced, 1.0850 g.). Ignition in air followed by rapid cooling in the tilted furnace yielded 64.0 mole % of PrO_2. This was the result of four runs, all of which agreed within 0.1 mg. The composition of the oxide obtained by ignition in air seems unaffected by the presence of small amounts of ceria.

This sample was next subjected to pressure oxidation. The results of these runs are shown in Table IV.

TABLE IV

RESULTS OF PRESSURE OXIDATION

Hours of heating	1.5	1.5	0.75	2.25
Lb. O_2/sq. in.	65	115	115	115
Temp., °C.	376–380	376–380	381–386	381–386
Mol. % of PrO_2	83.7	96.1	92.2	95.3

Experiments under practically similar conditions with ceria-free praseodymia showed, in the order of the runs above given, 67.9, 73.2, 71.0 and 76.6%. Thus it is seen that ceria causes an abnormally high degree of oxidation when the oxidation is accomplished under pressure.

The Attempt to Prepare Higher Oxides of Other Rare-Earth Elements.—Pressure oxidation of the sesquioxides of lanthanum, neodymium, samarium, gadolinium, erbium and ytterbium was investigated. Since it is universally recognized that the oxides of these elements are of the type R_2O_3, and cannot be reduced by hydrogen at temperatures ordinarily employed, it was considered unnecessary to include hydrogen reductions in these runs.

The ignition, cooling and weighing of the sesquioxides were carried out in purified air, with all the precautions previously described, since some of these oxides gain weight very rapidly on exposure to ordinary air. The attempts to produce oxides of type higher than R_2O_3 failed with all these elements, so tabulation of the runs may be omitted. Suffice it to say that in no case, with samples varying from 0.5 to 1.4 g., were increases greater than 0.3–0.4 mg. found, that is, increases of 0.03–0.06%, with the exception of erbium, in which an increase of 0.1% was registered. Since, however, we could not be certain of the complete absence of terbium, which admittedly forms a higher oxide, from this sample, we could not accept this slight gain in weight as evidence of any tendency toward higher oxide formation. The effective temperature ranges were covered, and pressures up to 405 lb. of oxygen were employed.

The interest attaching to the element terbium in its higher oxides, and the difficulty in getting enough of this element in a high state of purity, cause us to withhold our data obtained on a small sample of not established purity. It is hoped that this investigation will be finished later.

Discussion

Equilibrium which gives an oxide corresponding approximately to the formula Pr_6O_{11} seems to be rather rapidly attained, so that cooling from higher temperatures to ranges below 400" in an ordinary electric furnace produces this oxide from one of lower oxygen content, provided a sufficient supply of oxygen be present. The results in Table I, calculated to the basis of "mole % of Pr_6O_{11}" give, in the order there used, 100.3, 100.0, 100.0, 99.4, 96.7, 96.1, 95.8, 95.1, 95.1, 91.4 and 83.5%. These figures, considered with the experimental conditions described in the table, show clearly that there is a dissociation of this oxide above 700° (and probably somewhat below this temperature), but that re-oxidation occurs in cooling to below 400". Meyer, and Prandtl and Huttner, both state that Pr_6O_{11} is formed by heating at any temperatures between 500 and 900°, and assuming that the oxides were slowly cooled in the presence of plenty of air, this is just what our results would lead one to expect. But that a composition of higher oxygen constant than Pr_6O_{11} can be obtained, evidently in equilibrium, at temperatures around 390" we have shown by getting a constant composition of 68.1–68.3 mole % of PrO_2 when approaching from both sides, that is, from initial compositions of about 64 and 93%. A composition corresponding to 67.7 mole % of PrO_2 (which is 1% higher than theoretical for Pr_6O_{11}) seems to be in equilibrium at about 500°, since on successive heatings of twenty hours each at this temperature no change in composition was shown. It is probable, however, that in ordinary slow cooling insufficient time is allowed for the establishment of this equilibrium and therefore the composition corresponding to Pr_6O_{11} is found.

In the preparation of praseodymium dioxide by heating in oxygen we can offer no definite explanation of our failure to reach a purity higher than 99.2%. Curve C, of Fig. 4, shows that the complete oxidation of the last few per cent. of the oxide requires considerable time, and yet the results in Table III indicate that equilibrium had been reached at about 99.2%. It is unlikely that the dissociation pressure of this oxide exceeds 400 lb./sq. in. at the temperatures investigated. This would seem incompatible with our curve in Fig. 3, which shows that the pressure exceeds 215 lb. only when the temperature is raised above 405°. At 378° the longer the heating the higher the yield of PrO_2 at a pressure of 115 lb., while at 65 lb. pressure we get almost the same figure (around 68%) at 378° whether we heat for one hour or thirteen hours. This suggests almost complete dissociation of the dioxide at this temperature in pure oxygen at 65 lb. pressure, and Prandtl and Huttner found complete dissociation of the dioxide in inert gases, in oxygen and in air at atmospheric pressure at temperatures above 350°. Thus our results show clearly, as do also those of Prandtl and Huttner, that praseodymium oxide could not have been formed, as was claimed by Brauner and by Meyer, at 400° at atmospheric pressure.

The experiments with lanthanum, neodymium, gadolinium, erbium and ytterbium would surely have shown a tendency toward higher oxide formation if such tendency exists; failure to obtain positive results with these elements leads us to challenge the placing of any of these elements in a periodic group other than the third.

Summary

1. It has been shown that the composition of the oxide of praseodymium obtained by ignition in air varies with the conditions of ignition and cooling, but with a given set of conditions reasonably constant results are obtained.
2. Praseodymium dioxide of 99.2% purity has been prepared by heating lower oxides in pure oxygen at high pressures.
3. Data on the stability of praseodymium dioxide at different temperatures and pressures have been presented.
4. The effect of ceria in promoting higher oxide formation by praseodymium has been shown negligible at ordinary pressures, but quite marked in high concentrations of oxygen.
5. No higher oxides of lanthanum, neodymium, samarium, gadolinium, erbium and ytterbium could be formed.
6. A furnace generally applicable for the study of oxidation under

pressure and a balance and technique for the weighing of very hygroscopic substances have been described.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 186]

A FURTHER TEST OF THE RADIATION HYPOTHESIS

BY LOUIS S. KASSEL[1]

RECEIVED JULY 16, 1928 PUBLISHED JANUARY 8, 1929

Introduction

Since its statement by Perrin[2] the Radiation Hypothesis has been subjected to many experimental tests, with results that have been uniformly opposed to it. Its present position has been summarized by Daniels.[3] This recent rapid decline of the Radiation Hypothesis has been accompanied by the production of an improved theory of activation by collision. Christiansen suggested that the number of internal degrees of freedom of the molecule must be taken into account, and this suggestion was adopted by Hinshelwood[4] and by Fowler and Rideal,[5] who worked out a simple theory of what the former has called "quasi-unimolecular" reactions, that is, reactions which are unimolecular at high enough pressures, but whose rate begins to fall off at lower pressures. Several such reactions are known, as well as some whose rates have not been shown to decrease.

The theory of Hinshelwood was extended by Rice and Ramsperger,[6] and a second theory developed which was in better agreement with the facts; this differed from the former one only in assigning different specific reaction rates to activated molecules of different energy content. A somewhat similar theory, in equally good agreement with experiment, was worked out by the author.[7] Both Rice[8] and the author[9] have since given quantum theories of the effect, also, but without changing much the numerical results obtained. The position of these theories with respect to the experimental facts is that they can account quantitatively for the way in which the rate falls off with decreasing pressure in the decompositions of propionaldehyde, ethyl ether, methyl ether and azo-

---

[1] National Research Fellow in Chemistry.

[2] Perrin, Ann. *Physik*, 11, 5 (1919).

[3] Daniels, Chem. Rev., 5, 39 (1928).

[4] Hinshelwood, *Proc. Roy. Soc.*, 113A, 230 (1926).

[5] Fowler and Rideal, *ibid.*, 113A, 570 (1926).

[6] Rice and Ramsperger, THIS JOURNAL, 49, 1617 (1927); 50, 617 (1928).

[7] Kassel, J. *Phys.* Chem., 32, 225 (1927).

[8] Rice, *Proc. Nat. Acad. Sci.*, 14, 113, 118 (1928).

[9] Kassel, J. *Phys.* Chem., 32, 1065 (1928).

methane; they can also account for the fact that it has not fallen off noticeably at the lowest pressures studied with acetone, pinene and azo-*iso*propane; they can account for the decomposition of nitrogen pentoxide around atmospheric pressure without difficulty, a thing which the older theories were unable to do, and indeed down to about three mm. pressure; but Hibben[10] finds that the rate is maintained down to much lower pressures, 0.03 mm. at least. It is hard for the theories mentioned to account for more than 50% maintenance of the rate at this pressure, using kinetic theory diameters, such as are found satisfactory for the other substances. It would be possible to account for the results down to 0.03 mm. by using a "diameter for collisional deactivation" of 10^{-6} cm. The case for such large diameters has been stated by Bernard Lewis,[11] but the author, at least, is as yet reluctant to use them.

Thus, of all the unimolecular reactions known, nitrogen pentoxide is the only one whose rate causes any difficulty. It is possible to account for the variation of rate with pressure in all the other reactions quantitatively; more important for this comparison, there is a considerable margin of safety, so that if the rates were greater than they are, or were maintained to lower pressures, they could still be accounted for. In nitrogen pentoxide, on the other hand, if the method of activation is collisional, there seem to be a hundred times as many activations and deactivations as the theory allows. In searching for a way out of this difficulty, it occurred to the author that radiation, which has been shown to be without effect at higher pressures,[12] might still be the mechanism responsible for maintaining the rate at low pressures. The general reason why this would be so is that collisional activations and deactivations are of course bimolecular, while radiational ones are unimolecular; the latter would thus gain in importance as the pressure decreased. The results with azomethane and the other quasi-unimolecular reactions show that in these cases at least radiation has not become of importance in time to prevent the falling off in rate, and it is a little hard to see how enough radiation can be absorbed to be of much use, but it nevertheless seemed worth while to investigate the action of infra-red radiation on nitrogen peritoxide at low pressures.

Experimental Part

The most difficult problem in work of this character is to obtain a good source of light. Nernst glowers have been used, but, although they may be operated at a very high temperature, the actual area of the emitting surface is small; for this reason it seemed best to use some other source. The one adopted was a rod of a substance whose trade name is "Glowbar" and which is used as the heating element in some of the small

---

[10] Hibben, *Proc. Nat. Acad. Sci.,* 13,626 (1927); THIS JOURNAL, 50, 940 (1928).

[11] Bernard Lewis, *Science,* 66, 331 (1927).

[12] Daniels, THIS JOURNAL, 48,607 (1926); Taylor, *ibid.,* 48, 577 *(1926).*

domestic electric heaters now in common use. This is a black substance of unknown composition, with a rather fine granular structure; it has a moderately high electric resistance, and may be conveniently heated by the passage of a current through it. A piece 20 cm. long and 9 mm. in diameter was ground down to about 6 mm. diameter in the central 4 cm. It was shielded along most of its length by a hollow fire-clay cylinder, to reduce heat losses; this had a rectangular opening, 1.5 X 3.6 cm., cut in it to serve as a source of light. The ends were mounted in heavy brass electrodes cooled by a blast of air and a potential of 220 volts was applied. The entire central portion, both the rod and the surrounding cylinder, attained an intense white heat, while the constricted portion of the rod reached a temperature evidently considerably greater.

It seemed almost impossible to place a reaction vessel within a few cm. of a source such as this and prevent it from heating up, and accordingly the light was focused some distance away by a simple optical system. A concave mirror of 30.5 cm. radius of curvature and 20.3 cm. diameter was placed at a distance of 60 cm. from the source; the reflected light was intercepted by a small plane mirror placed about 17 cm. from the large mirror and making an angle of 45° with the path of the light; this second mirror reflected the light down, and it came to a focus upon the window of the reaction vessel. Both mirrors, of course, were silvered on their outer surfaces. The energy flux through the window was determined by absorbing the radiation in a 2% solution of cupric chloride, which absorbs everything beyond 0.6μ. As the mean of a number of determinations made in this way, there was obtained the value 6.2×10^7 ergs/sec. It was estimated that the temperature of the rod was 2200°K. and that of the protecting cylinder 1800°. Using those figures, and those given for the dimensions of the apparatus, it is possible to calculate the energy flux which would be expected; it is found to be 6.6×10^7 ergs/sec.; if the lower temperature is taken as 1700°, the expected flux comes out 6.0×10^7 ergs/sec. This shows that the temperatures assumed are approximately correct. If the enclosure was all at a uniform temperature of 1900°, it would produce a flux of 5.5×10^7 ergs/sec., and at 2000° one of 6.7×10^7 ergs/sec. In all of these calculations the losses on reflection at the mirrors and transmission by the window have been neglected. The necessary corrections could be made, but they would not change the conclusions in any way.

The reaction vessel used was a 250-cc. bulb; the neck was cut off near the bulb and ground very carefully; a window of rock salt, which has very good transmission in the infra-red region, was attached by sealing wax, care being taken to get the wax only on the outer edge, so that the contact with the reacting gas would be very poor; no visible change took place in the sealing wax, nor was there any other reason to suspect that an appreciable amount of reaction was occurring at the window. The bulb was placed in a jar, which was filled with water or ice and water to a point just below the window, during all of the runs. The pressure readings were obtained by a bifilar quartz fiber gage and were at all times accurately reproducible.

The nitrogen pentoxide was prepared by letting nitrogen dioxide vapor diffuse into a stream of ozonized oxygen and passing the resulting gases through a trap cooled to about −50°. It usually required about ten minutes to collect sufficient nitrogen pentoxide for a run. The supply of nitrogen dioxide would then be sealed off and the ozone continued for a few minutes longer; then it, too, would be sealed off. The nitrogen pentoxide was next cooled with liquid air and connected through a stopcock to a two-stage mercury vapor pump, a second liquid-air trap preventing diffusion of any mercury vapors into the apparatus. After the pumping had been continued for some time, and a vacuum of 10^{-5} mm. or better obtained, the jar around the reaction vessel was filled with ice and water, the liquid air surrounding the nitrogen pentoxide replaced by a mush of frozen ethyl acetate (−83.6') and the pumping continued; after some time, usually about one-half hour, the liquid air was replaced, and the apparatus sealed off from the pumps; at this stage it consisted merely of the reaction bulb, the fiber gage, and the trap containing solid nitrogen pentoxide. The residual pressure was then read on the fiber gage, after which the liquid air was replaced by the ethyl acetate mush, and the decomposition allowed to proceed thermally for a definite period; the liquid air was then replaced and after equilibrium had been reached the pressure was again read; the increase represented oxygen liberated by the decomposition; the source of infra-red light was then turned on, the ethyl acetate replaced and the reaction allowed to proceed for the same period as before, after which liquid air was replaced and the pressure read. Runs were made alternately with and without the light in this fashion.

There was no heating of the bulb when the light was on and except for the presence of the radiation all conditions were unaltered. Hence it is only necessary to compare the pressure increases during the period with illumination with those without to see whether radiation has had an effect. In some of the later runs solid chloroform (–63.5°) was used as a refrigerant and the reaction vessel was kept at 25° instead of at 0°. This gave pressure increases which were considerably larger and easily measurable, so that the same relative increase in rate could have been more easily detected than before. On the other hand, it made conditions less favorable, so that a smaller relative increase was to be expected.

The usual period of each run was thirty minutes, though some were shorter. With ethyl acetate as a refrigerant and the reaction vessel at 0° no pressure increase was ever noted except on one occasion, which was afterward found to be due to a leak which developed at the window. With chloroform and the reaction vessel at 25°, the pressure increases found with illumination were no greater than those without. A typical set of results under the latter conditions is: initial pressure, 0.00035 mm.; increase, dark, 0.00141; increase, light, 0.00147; increase, dark, 0.00153; increase, light, 0.00140. The third figure is not accurate, the probable error being of the order of the fluctuations in the values given. Similar results were found on several occasions. There was no evidence that infra-red radiation influences the rate of reaction of nitrogen pentoxide under the experimental conditions used, although a 10% increase in rate could have been definitely detected.

The vapor pressure equation of Daniels and Johnston[13] gives a pressure of 0.00068 mm. at –83.6° and one of 0.0245 mm. at –63.5°.

A simple calculation shows that the reaction rate constant found in the experiment quoted is about the same as that at higher pressures. This is not to be regarded as a measurement of the thermal rate at low pressures, however, since the experimental conditions did not permit absolute rate measurements. Thus it was impossible to bake out the reaction vessel; the possibility of slight reaction with the sealing wax is not excluded; adsorption on the walls may have affected the pressure measurements. Due to the comparative method used, it is not believed that any of these objections affect the conclusions as to the inactivity of radiation.

Discussion

It having been found that under the experimental conditions used no additional reaction was produced, it becomes important to decide for what spectral region the test is significant. This may be done by comparing the amount of radiation present in the reaction bulb normally with the amount introduced at various wave lengths. The calculation has been made for the rod at 2200°K. and the protecting cylinder at 1700°K., and also for the entire area at 1900°K. This may be very

---

[13] Daniels and Johnston, THIS JOURNAL, 42, 1131 (1920).

easily done from a knowledge of the geometry of the apparatus, assuming that the source of light behaves as a black body, The volume of the reaction system was taken as 300 cc. and the average length of path of the light through the nitrogen pentoxide as 12 cm. Absorption by the nitrogen pentoxide was neglected. It was found that at 5μ the average intensity in the reaction system was increased about 7 times when the vessel was at 0° and 3 times when it was at 25°. Nearly the same result was obtained whether the calculation was made for the rod at 2200°K. and the cylinder at 1700° or for both at 1900°. It is possible that the use of the black body law is not justified, but in that case the actual temperature of the source must have been greater, and the amount of radiation in the far infra-red would scarcely be much less than that calculated. For wave lengths shorter than 5μ the relative increase is much greater, while for only slightly longer wave lengths the increase is too small to be significant. Therefore this test applied only to wave lengths of 5μ and less. Since in the experiments at 25° a 10% increase in rate would have been observed, and was not, and since the intensity of all wave lengths less than 5μ was increased at least 3 times, one is tempted to say that not more than 3% of the thermal reaction at this temperature can depend upon radiation of this spectral region. Closer analysis, however, shows that this statement is unjustified, and it is necessary to be content with the milder conclusion that not more than 3% of the total thermal reaction can be caused exclusively by radiation of wave lengths less than 5μ.

Now there is no difficulty about the production of any except the more highly activated molecules. Collisions are quite capable of accounting for the maintenance of the Maxwell-Boltzmann quota of all the unactivated molecules and even of the activated molecules of low energy content; these, however, do not contribute very much to the total reaction. Thus if radiation is to be of any help, it must produce the final activation, that is, it must keep up the quota of highly activated molecules. If radiation of the wave lengths tested was able to do this effectively, a considerable increase in the reaction rate would have been obtained. The experiments do not show that this radiation is unable to produce highly activated molecules, but they do seem to show that in the actual thermal reaction it is not the important agency in their production. There remains the possibility that radiation of longer wave lengths is of importance. A quantum even at 10μ corresponds to about 3000 calories per mole, which is far from negligible; the addition of that much energy to a molecule just barely activated, which has very little chance to react, will convert it into one which will probably decompose before its next collision. Still longer waves may be of some use, but it is hard to believe that they can be the really important factor in the reaction. It would seem that the final hope of the Radiation Hypothesis rests in the region from 5 to 10μ. Even here it is difficult to understand how sufficient radiation can be absorbed to maintain the rate. Some calculations which have been made by Dr. Ure, in this Laboratory, seem to show that radiation is doomed to fall short by a factor of about 100; these calculations have taken into account the internal degrees of freedom of the molecule and are about as favorable to radiation as seems at all reasonable.

Thus the decomposition of nitrogen pentoxide at low pressures remains mysterious. There are a hundred times too few collisions to account for the rate; there does not seem to be any help from radiation of wave lengths less than 5μ, and it is hard to see how radiation of any wave length can account for more than a very few per cent. of the reaction. There are apparently three possible explanations of the difficulty. One is that the low pressure experiments have been incorrectly interpreted, due perhaps to adsorption; there is evidently some feeling in various quarters that this is the proper solution, but the burden of proof surely rests upon those who wish to adopt this view. Another is to assert that the long wave length radiation is responsible, even though it is impossible to give a theoretical explanation of how it can be. It seems very hard to test this view, a suitable source being non-existent. A third escape is in the acceptance of diameters for collisional deactivation of about 10^{-6} cm. It has been said that the use of a large diameter for deactivations does not mean that an equally large one is required for other collisions, in particular for activations. Let us examine this statement closely. A large diameter for deactivations means that the high-energy molecule has a very great desire to get rid of its extra energy. The result of this large diameter is that the number of deactivations is increased; to maintain the Maxwell-Boltzmann quota of high energy molecules an increased number of activations is required, and these may be obtained either by a large diameter for activations also, or by an abnormal tendency to produce activation whenever it is energetically possible, that is, by having nearly all of the energy of both molecules flow into one of them oftener than the distribution laws for harmonic oscillators would require. The existence of equilibria maintained in this last way is denied by the Principle of Microscopic Reversibility. According to this principle, if the mechanism of deactivation is the transfer of energy across distances large compared to molecular dimensions, the mechanism of activation must be of the same nature.[14] The author has been among those guilty of talking about diameters for collisional deactivation, with the implication that they might be much larger than other diameters. But if we are going to use large diameters for internal energy transfers, it would be better to use them consistently. It would of course be possible that the diameter for

---

[14] See also Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, 13, 188 (1927).

such transfers might be a function of the amount of energy involved; but in the application of the author's theory to azomethane the chief difficulty was to get sufficient spread between the theoretical curves at different temperatures; the same trouble was experienced by Rice and Ramsperger; if the diameter for internal energy transfers increased very much with the amount of energy involved in this case, it would become impossible to fit the experimental data. If, as therefore seems not unlikely, the diameter for internal energy transfer is approximately independent of the energy, and if it is really much larger than kinetic theory diameters, the heat conductivity of nitrogen pentoxide should be abnormally large. There do not seem to be any data on this.

As a matter of fact, it seems rather strange to speak either of collisions or of diameters in connection with energy transfer at such a distance, for the phenomenon, if it occurs, is more nearly "coupling" of the type suggested by Polanyi,[15] with the difference that the result of the energy transfer is only activation, not immediate dissociation.

In this connection it may be pointed out that the chief objection to these "large diameters" is not an a *priori* one, since they are not inherently unreasonable (at least, not until they are somewhat greater than 10^{-6} cm.) but is based on a reluctance to use diameters for nitrogen pentoxide at least 15–20 times greater than for any of the other substances which decompose unimolecularly, but there is apparently some feature about nitrogen pentoxide which is unique, so that some abnormality in the explanation of its rate can scarcely be avoided.

Since the submission of this paper, Rice, Urey and Washburne[16] have found that a molecular ray of nitrogen pentoxide is not decomposed by black body radiation. Loomis and Smith[17] have reported experiments which seem to show that under some circumstances adsorption may vitiate low pressure reaction rate measurements on nitrogen pentoxide. Sprenger[18] has found the very curious result that at low pressures the decomposition of nitrogen pentoxide does not go to completion, even at 100°; and Rice, Urey and Washburne[16] mention that preliminary experiments in their Laboratory show a falling off in rate even at several millimeters' pressure. Thus five separate researches on the thermal reaction at low pressures have led to five widely different conclusions.

This investigation was aided financially from a grant made to Professor **A. A.** Noyes by the Carnegie Institution of Washington. The author wishes also to express his appreciation of the advice and assistance which he received from many members of the staff of the Chemistry Depart-

---

[15] Polanyi, *Z. Physik*, **3**, 31 (1926).

[16] Rice, Urey and Washburne, THIS JOURNAL, **50**, 2402 (1928).

[17] Loomis and Smith, *ibid.*, **50**, 1864 (1928).

[18] Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

ment, in particular Professor R. C. Tolman and Dr. M. E. Nordberg. The very excellent rock salt windows used were kindly furnished by Mr. Rene Engel of the Geology Department of this Institute.

Summary

1. It has been suggested that the maintenance of rate in the decomposition of nitrogen pentoxide may be due to assistance from radiation, which becomes important only at low pressures.

2. It has been found experimentally, however, that radiation of wave length less than 5μ is not able to increase the reaction rate even at low pressures.

3. It is concluded that the important region, if there is any, will probably lie between 5 and 10μ, but that it is hard to see how enough radiation can be absorbed to maintain the rate. An experiment which might detect this activity, if it exists, has been suggested.

4. The other possible escapes from the nitrogen pentoxide dilemma have been considered. No definite conclusion has been reached.

BERKELEY AND PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES OF COPPER CATALYSTS PREPARED FROM PRECIPITATED HYDROXIDE. I.
ACTIVITY AS A FUNCTION OF THE TEMPERATURE OF PRECIPITATION

BY PER K. FROLICH, M. R. FENSKE AND D. QUIGGLE

RECEIVED JULY 19, 1928 PUBLISHED JANUARY 8, 1929

In the course of a study of the high pressure synthesis of methanol undertaken by this Laboratory some three years ago, it was observed that certain catalysts prepared from precipitated hydrates showed variations in activity which might be attributed to differences in the temperatures at which the hydrates had been precipitated from the corresponding nitrate solutions. To obtain more quantitative information concerning this temperature effect, a series of experiments was made with copper catalysts under carefully controlled conditions in order to eliminate in so far as possible the effect of variables other than the temperature of precipitation. The copper hydroxide was precipitated with ammonium hydroxide from aqueous solution of one of the standard makes of high purity (C. P.) copper nitrate. Since any occluded ammonium hydroxide or nitrate was easily volatilized in subsequent operations, the resulting catalysts might be expected to be of identical chemical composition.

Six different temperatures of precipitation were used, *viz.*, 0, 10, 22, 55, 85 and 100°.

Preparation of Catalyst and Experimental Procedure.—One hundred grams of copper nitrate crystals ($Cu(NO)_3\cdot 3H_2O$) was dissolved in **1500** cc. of water and heated or cooled to the temperature chosen for precipitation. An ammonia solution containing one part by volume of concentrated ammonia (sp. gr. **0.89)** to two parts of water, was brought to the same temperature and added to the nitrate solution at a constant rate of **20** cc. per minute until a faintly alkaline reaction was obtained. During the precipitation the solution was continuously agitated by a motor-driven stirrer. The hydroxide was allowed to settle and then washed three times by decantation, each time using one liter of distilled water at the same temperature as that used in the precipitation. In some cases the third settling was very slow and the gel was therefore placed on the suction filter. After washing on the filter with a fourth liter of water at the same temperature, the gel was transferred to an electric oven and dried at 110°. In order to remove any occluded ammonia salts, the hydroxide was then heated at **220**° for four hours in a stream of nitrogen. By this procedure the hydroxide was converted into copper oxide.

The apparatus was exactly the same as that employed in previous studies on methanol catalysts and described in detail elsewhere.[1] It consisted essentially of an electrically heated pyrex tube in which the catalysts were exposed to methanol vapor supplied at a constant rate of flow. At the exit end of the apparatus means were provided for collecting the products of reaction, that is, formaldehyde, methyl formate and gaseous products.

A fixed amount of copper oxide, **0.43** g., prepared as above by heating at 220°, was reduced by passing over it **0.0462** mole of methanol at the lowest temperature at which reduction could be made to take place, varying between **190** and **210**°. The resulting catalyst was then raised to operating temperature, 360°, and **0.1156** mole of methanol vapor passed over it at a constant rate of flow for a period of ninety-three minutes. Formaldehyde and methyl formate were absorbed in low-head scrubbers containing water and methanol, while the gaseous products, consisting of hydrogen, carbon monoxide, carbon dioxide and methane, were collected in a graduated gasometer. All analyses were made according to standard methods.[1]

Discussion of Results.—The percentage of methanol decomposed as a function of temperature of precipitation is shown in Fig. 1, plotted from the data in Table I. It is seen that the maximum decomposition occurs with the catalyst prepared by precipitating the hydroxide at 22° and that this point stands out markedly from the others, corresponding to a five-

TABLE I

RESULTS OF EXPERIMENTS

		Methanol decomposed occurring as		
Precip. temp.. °C.	**Methanol decomposed, %**	**Formaldehyde, %**	**Methyl formate, %**	**Carbon monoxide, %**
0	2.5	83.2	15.9	0.2
10	5.3	77.8	19.8	.5
22	12.3	45.5	51.2	1.2
55	6.9	75.0	23.8	0.5
85	8.8	55.0	41.2	2.0
100	8.4	61.2	36.2	1.0

---

[1] Frolich, Fenske and Quiggle, Ind. *Eng. Chem.*, **20,694 (1928).**

fold increase in activity over the catalyst resulting from precipitation at 0°. Another catalyst prepared by the same procedure gives a perfect check of the 22° point, and the entire general shape of the curve is checked in another series of experiments using smaller amounts of catalyst.[2]

As already mentioned above, these results were obtained with constant weights of catalyst. However, the specific volumes of the copper oxide samples and of the resulting catalysts were rather constant throughout, and hence the shape of the decomposition curve in Fig. 1 cannot be explained on the basis of variations in the time of contact of methanol vapor with the catalysts. Furthermore, it was observed that the more active the catalyst the lower the temperature required to start reduction. This initial reduction temperature is an inherent property of the copper oxide; it seems to be the result of the catalytic activity of the substance in question, rather than the cause, although it is of course impossible to distinguish completely between the two effects. The variation in the temperature of reduction is undoubtedly closely associated with the chemical composition and physical structure of the gels from which the catalysts are prepared. That the gels precipitated at various temperatures vary profoundly in these respects, is apparent from the following observations. The low temperature hydroxides are blue, while those precipitated at higher temperature are black, with a gradual transition in color between the two extremes. The gels resulting from low temperature precipitation

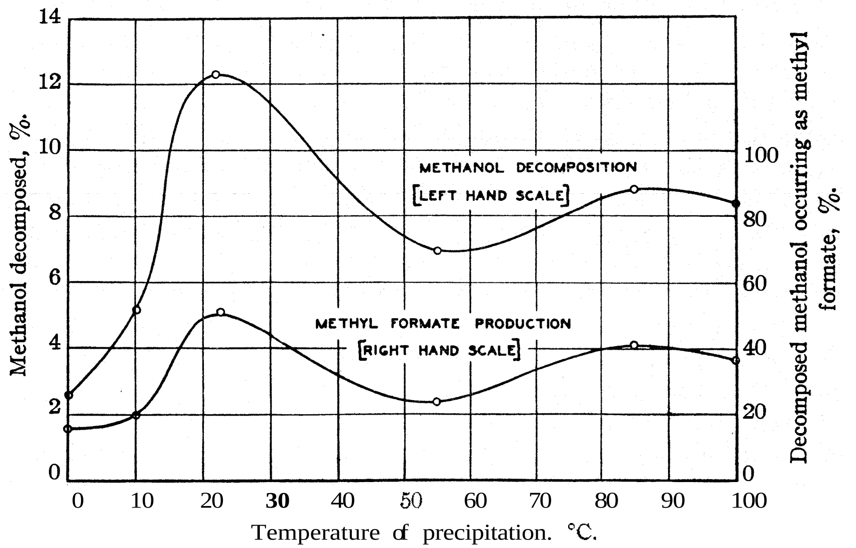


Fig. 1.—Data on copper catalysts prepared from the ammonia precipitated hydroxides, showing activity as a function of temperature of precipitation.

---

[2] G. L. MacLaughlin, M. I. T. "Thesis," 1927.

are also much more hydrated and bulky than those obtained at high temperature.[3]

Interesting light is also thrown upon the character of the gels by means of x-ray analysis. The gels precipitated at 85° and higher temperatures consist essentially of copper oxide with only small amounts of hydroxide. As the temperature of precipitation decreases, the amount of copper hydroxide present in the dried gels increases, until finally the material obtained by precipitation at 30°, or lower, shows only faint indications of copper oxide. The particle size of the dried gels is quite small and, in a qualitative way, the x-ray pictures indicate smaller gel particle size to be associated with the more active catalysts.

Based on these admittedly qualitative data on particle size, an explanation of the decomposition curve in Pig. 1 may be offered. Thus it seems that the particle size of the hydroxides decreases with decreasing temperature of precipitation, but at the same time the degree of hydration increases markedly. When the resulting gels are subsequently dried at 110° there is a tendency for the particle size to increase, as is commonly observed in analytical chemistry when highly insoluble precipitates as, for instance, barium sulfate and calcium oxalate, etc., are left wet for a few hours at 80 to 100°. However, since it takes a longer time for the water to be removed from the highly hydrated low temperature gels, these particles will have more chance to grow than will the particles precipitated at the higher temperature and containing practically no water of hydration. The result is that the final particle size of the dried gel is determined by two opposing factors: (1) the tendency for the initial particle size to decrease with decreasing temperature of precipitation, and (2) the tendency for the initially formed particles to grow while the drying proceeds at 110°. This might well explain the occurrence of a minimum particle size corresponding to a temperature of precipitation of about 22°. It may then be assumed that the particle size of the dried gel determines the activity of the catalysts resulting from subsequent reduction, either by determining the size of the catalyst particles or their form. This line of reasoning is further substantiated by the work of MacLaughlin,[2] showing that the most active catalyst results by precipitation at 0° when the gels are dried at room temperature (25°), rather than at 110°, as was done in this series of experiments.

The particle size of the metallic copper catalysts, in contrast to the gel from which they are prepared, is relatively large, a result which might be expected because there is no foreign material present to interfere with growth of crystals during the reduction process. However, x-rays fail to

---

[3] An interesting discussion of the various hydrated copper oxides or hydroxides is given by H. B. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, p. 134.

disclose any perceptible difference in particle size of the individual catalysts.

From the data in Table I it will be seen that these catalysts decompose methanol largely into formaldehyde, but that considerable methyl formate is produced simultaneously. The more active the catalyst the larger is the percentage of decomposed methanol occurring as methyl formate, as shown in Fig. 1.[4] Apparently this effect of the active catalysts producing mainly methyl formate is characteristic of promoted copper, as has already been demonstrated to be the case for mixtures of copper and zinc oxide.' A similar effect is observed when alkali is used as a promoter, as will be shown in the second paper of this series.

Acknowledgment.—The data presented here are abstracted from a considerable amount of experimental work conducted in the Research Laboratory of Applied Chemistry during the past years. The writers are indebted to Messrs. G. L. MacLaughlin and R. O. Spurdle for preparation of some of the catalysts discussed, and to Mr. W. C. Asbury who obtained the x-ray data in cooperation with Dr. G. L. Clark.

Summary

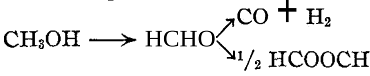
The activity of copper catalysts prepared from the ammonia precipitated hydrate varies markedly with the temperature of precipitation. There appears to be a maximum in activity corresponding to a temperature of precipitation in the neighborhood of 22".

On the basis of x-ray examination of the dried gels prior to reduction, it is suggested that the activity is determined by the particle size at this stage in the catalyst preparation. An explanation is also attempted to account for the apparent minimum in particle size of the gels precipitated at about 22°.

CAMBRIDGE, MASSACHUSETTS

---

[4] Roughly, the methyl formate curve runs parallel to the activity curve, the curve for formaldehyde (not plotted) being the reverse of the methyl formate curve. No doubt the methyl formate is a polymer of formaldehyde formed in accordance with the following scheme for the decomposition of methanol



$$CH_3OH \longrightarrow HCHO \begin{cases} \nearrow CO + H_2 \\ \searrow {}^1/_2\ HCOOCH_3 \end{cases}$$

That aldehydes can polymerize to form esters is well known [Mannich and Geilmann, *Ber.*, **49**,585 (1916)] and this same type of reaction is apparently employed for the production of butyl butyrate by dehydrogenation of butyl alcohol by means of copper catalysts [U. S. Patent 1,580,143, April 13, 1926].

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

SOLUBILITY. XII. REGULAR SOLUTIONS[1]

BY JOEL H. HILDEBRAND

RECEIVED JULY 23, 1928 PUBLISHED JANUARY 8, 1929

In a systematic study of deviations from Raoult's law, or other relations which may be derived from it, the author[2] has made much use of solubility data for solids and has shown that, particularly among substances of low polarity, there exist families of solubility curves which bespeak a marked regularity even where the deviations are very large. Evidently, the equations for the curves belonging to these families for systems which we will call ***regular***, are to be sought before those of divergent and often highly individualistic curves, shown by ***irregular*** systems. In the case of iodine, for example, the solvents which give a violet color, similar to that of iodine vapor, give regular solubility curves, while the solvents which give brown solutions give irregular curves. Fig. 1, giving solubility curves for stannic iodide in various solvents found by plotting log N_2, where N_2 is the mole fraction of the solute, against $1/T$, illustrates such a family of regular curves. It has been easy to show that the positions of the curves accord fairly well with the differences in internal pressure between the solvents and the solute, but it has not heretofore been possible to get from the solubility data as a whole any simple measure of the deviations from Raoult's law, for the spacing of the curves depends upon the distance from the melting point of the solute.

Mortimer,[3] it is true, has given an approximate treatment by assuming that the solubility curves are straight lines converging to the melting point, the slopes representing the heats of solution calculable upon an additive basis from a table of relative internal pressures. While this treatment is practically useful for systems deviating but moderately from Raoult's law, it is unsatisfactory, first, because the solubility curves are not linear, as Mortimer himself recognized; second, because where the solute melts to give a second liquid phase, its solubility curve does not converge to the melting point, but behaves as does heptane in Fig. 1; and, third, because the slope of the solubility curve does not, in general, give directly the partial molal heat of solution but requires a correcting term to be discussed later.

The course of the solubility curve for a solid depends upon the variation

---

[1] A brief preliminary paper has been published in the *Proc. Nat. Acad. Sci.*, 13, 267 (1927).

[2] (a) Hildebrand, THIS JOURNAL, a series of ten papers beginning in 1916, *cf.* "Bibliography," ref. 2b, p. 200; (b) Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, New York, 1924; (c) ref. 2(b), Chap. XIV, see also Dorfman and Hildebrand, THIS JOURNAL, 49, 729 (1927).

[3] Mortimer, THIS JOURNAL, 44, 1416 (1922); 45, 633 (1923).

in its activity with both composition and temperature. Margules[4] long ago suggested for the variation in activity, a_2, with mole fraction, N_2, of Component 2 of a binary liquid mixture, the expression

$$\ln a_2 = \ln N_2 + {}^1/_2\beta_2 N_1^2 + {}^1/_3\gamma_2 N_1^3 + \ldots..$$

and, similarly, with subscripts interchanged, for the other component. Porter[6] called attention to a fact that had also been noted by the writer, *i. e.*, that terms higher than N^2 may be omitted for many systems. In 1906, van Laar[6] gave an equation based upon the van der Waals equation of state for mixtures, which in our notation reads

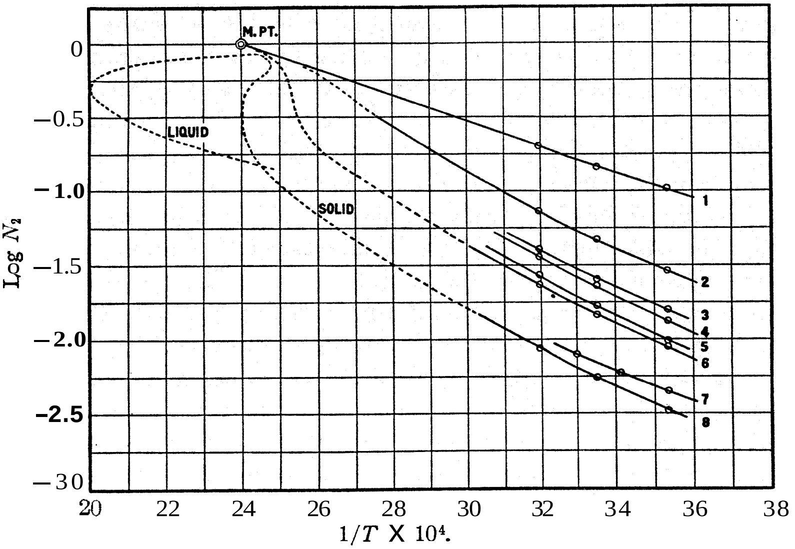


Fig. 1.—Solubilities of stannic iodide in: 1, carbon disulfide; 2, ethylene bromide; 3, m-xylene, 4, benzene; 5, chloroform; 6, carbon tetrachloride; 7, ether; 8, heptane.

$$RT \ln a_2 = RT \ln N_2 + \alpha N_1^2/(1 + rN_1)^2$$

where α and r are functions of the van der Waals "constants." When the van der Waals "b" is the same for the two components this reduces to

$$RT \ln a_2 = RT \ln N_2 + \alpha N_1^2$$

The term αN_1^2 is intended to represent the partial molal heat of mixing, and would be independent of temperature if the van der Waals equation were strictly applicable.

More recently van Laar and Lorenz[7] have published a derivation of

---

[4] Margules, *Sitzb. Wien. Akad.*, [2] *104,* 1243 (1895).

[5] Porter, *Trans. Faraday Soc.*, *16,* 336 (1921).

[6] Van Laar, "Sech Vorträge über das thermodynamische Potential," Vieweg und Sohn, Braunschweig, 1906; *cf.* also *Z. physik.* Chem., **72,**723 (1910).

[7] J. J. van Laar and R. Lorenz, *Z anorg. allgem* Chem., ***145,**239* (1925).

the above equation. Experimental tests of their equations have rarely been made by the van der Waals "school" beyond the mere citing of systems which conform as to type, and the present case is no exception. It is also unfortunate that the generally accurate thermodynamic methods employed in Holland have been so inextricably bound up with an inadequate equation of state.

Shortly before the publication of the previous paper by the writer on this subject, there appeared an important paper by Heitler[8] in which the simplified equation given by van Laar was derived without reference to the van der Waals constants, by considering the solution as a lattice, examining the probability of the various arrangements of the two molecular species therein, and by the aid of certain other assumptions that cannot be repeated here. He tested the formula by showing that the isotherms for the vapor pressure of five mixtures can be calculated with fairly good agreement by getting the heat of mixing from the curve itself, although the agreement with the experimental heat of mixing was not at all good. He further applied the formula to the calculation of the liquid–liquid solubility curve, and tested it with existing data for eight systems, finding that the experimental curves are in all cases somewhat flatter.

Most of the systems cited by Heitler involve one more or less polar constituent and one involves solvation. The writer believes it to be important in this connection to distinguish the systems here designated as regular from those involving solvation or association, in order to gain a correct prediction of the temperature effect, and also that the change in volume on mixing should be taken into consideration. The following simple considerations are advanced regarding the entropy of regular solutions.

If a solution is ideal, in the sense of obeying Raoult's law, the change in free energy corresponding to the transfer of a mole of component X_2 from the pure liquid state to a large amount of solution, in which its mole fraction is N_2, is[9]

$$\bar{F}_2^i - F_2^\circ = RT \ln N_2 \tag{1}$$

The corresponding entropy change is

$$\bar{S}_2^i - S_2^\circ = \frac{d(\bar{F}_2^i - F_2^\circ)}{dT} = R \ln N_2 \tag{2}$$

which thus depends upon composition only. From the standpoint of the interpretation of entropy in terms of probability, we can say that a mixture represents a more probable state for such a system than do the separate liquids. Now suppose that the component X_2 is transferred from an ideal solution to any regular solution in which it has the same

---

[8] Heitler, *Ann. Physik,* [4] 80, 630 (1926).

[9] Ref. 2b, p. 29.

mole fraction. From our picture of a regular solution as one in which orienting and chemical effects are absent, and in which the distribution and orientations are random, just as in the ideal solution, we may conclude that the probability of X_2 is the same in the two solutions and, therefore, that the difference in entropy is zero. We cannot expect this conclusion to hold unless the random distribution of the molecules persists. We may expect, further, that a small correction should be applied to take care of the change in entropy accompanying changes in volume, given by

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (3)$$

or we may state our principle in the following form. *A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged.* Let us examine the consequences of this simple postulate.

When one mole of X_2 is transferred from the pure liquid to a regular solution, the change in free energy is

$$\bar{F}_2 - F_2^{\circ} = RT\ ln\ a_2 \qquad (4)$$

where a_2 is the activity of X_2 in the solution referred to the pure liquid as the standard state, The change in free energy in transferring one mole of X_2 from the ideal solution to a regular solution is found by subtracting Equation 1 from Equation 4, giving

$$\bar{F}_2 - \bar{F}_2^{1} = RT\ ln\ \frac{a_2}{N_2} \qquad (5)$$

The corresponding entropy change is zero, according to our postulate, except for the volume correction, hence the right-hand member of Equation 5, as a first approximation, is not a function of temperature, and is equal to the partial molal heat of mixing

$$\bar{F}_2 - \bar{F}_2^{1} = \bar{H}_2 \qquad (6)$$

This is, however, a function of composition, the approximate form of which has been derived by Heitler as parabolic. This follows, also, in a less rigid way, from the following simple considerations. The excess of heat content of a mole of regular solution over an ideal solution, AH, may be expected to be greatest in an equimolal mixture, falling off continuously to zero at the ends, as shown in Fig. 2. A simple equation for the course of such a curve is $AF = bN_1N_2$, where b is a constant. Since $N_1 + N_2 = 1$, either mole fraction could be eliminated, but we prefer to keep the symmetrical form. From the definition of partial molal quantities, it follows that

$$\bar{H}_2 = bN_1^2, \text{ and } \bar{H}_1 = bN_2^2 \qquad (7)$$

Substituting in Equation 5 by the aid of 6, we get

$$RT\ ln\ \frac{a_2}{N_2} = bN_1^2 \qquad (8)$$

and the same, with subscripts interchanged, for the other component. One may prefer to express a_2/N_2 as γ, the activity coefficient.

The parabolic shape of the exponential term is illustrated by figures in Ref. 2b, pp. **43,** 49 and **63.**

In cases where the system proves unsymmetrical, we may add higher powers of N_1 and write Equation 8 as

$$\ln \frac{a_2}{N_2} = \frac{1}{RT}\,(bN_1^2 + cN_1^3 + \ldots\ldots) \tag{9}$$

where b, c, etc., are not functions of temperature, except for the correction due to volume changes, which we shall, in general, neglect. The corresponding equation for the other component then becomes, by the aid of the Duhem equation

$$\ln \frac{a_1}{N_1} = \frac{1}{RT}\left(b + \frac{3}{2}\,c\right)N_2^2 + cN_2^3 + \ldots\ldots \tag{10}$$

We will examine extensive experimental evidence in support of this formulation, using the simpler Equation 8, so far as possible.

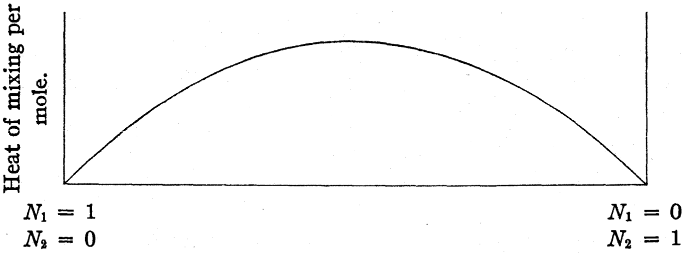


Fig. 2.—Relation between mole fraction and heat of mixing per mole.

Solubilities in Regular Solutions.—We can test Equation 8, first, by the use of solubility data, provided that they cover a considerable range in temperature. Since the activity of the solute, a_2, is the same in its saturated solutions in all solvents, including those in which it obeys Raoult's law, we may write $a_2 = N_2^i$, where N_2^i is the solubility in the ideal solution, which can be calculated by the aid of a knowledge of the melting point and heat of fusion of the solute. Equation 8 thus becomes

$$\ln \frac{N_2^i}{N_2} = \frac{bN_1^2}{RT} \tag{11}$$

which may be written

$$\log \frac{N_2^i}{N_2} = \frac{kN_1^2}{T} \tag{12}$$

where $k = 0.4343b/R$.

We will first apply this equation to data upon the solubility of sulfur in various solvents published by Hildebrand and Jenks,[10] together with

---

[10] Hildebrand and Jenks, THIS JOURNAL, 43, 2172 (1921); *cf.* also ref. 2b, p. 151.

some data by Étard reproduced in the same paper. Table I contains values for 100 N_2, the mole per cent. of sulfur in the solutions, and the corresponding value of k calculated from the solubilities. It will be seen

TABLE I

VALUES OF $k = b/2.303R$ FOR SULFUR SOLUTIONS

Solvent	*t*	0	25	35	45	54	Mean *k*	
CCl_4	100N_2	0.203	0.500	0.697	0.966	1.212		
	k	529	529	528	527	528	528	
C_7H_{16}	100N_2	0.0484	0.1413	0.2005	0.274	3.363		
	k	696	688	689	693	694	692	
$C_6H_5CH_3$	100N_2	0.324	0.734	0.995	1.330	1.797		
	k	474	479	483	483	480	480	
m-$C_6H_4(CH_3)_2$	100N_2	...	0.825	...	1.523	...		
	k	...	466	...	475	...	471	
	t	9	22	40	50	72	95	Mean k
$C_2H_4Br_2$	100N_2	1.253	1.77	3.26	4.77	9.42	24.05	
	k	354	331	356	342	339	334	343
	t	8	21	39	65	72	100	
C_6H_6	100N_2	0.368	0.557	1.029	2.18	2.79	6.07	
	k	493	498	495	497	487	485	493
	t	24	43	54	61	74	85	
$(C_2H_4Cl)_2S$	100N_2	0.922	1.525	2.13	2.72	3.88	5.87	
	k	448	458	456	450	452	(439)	453

that, in spite of the large variations in N_2 and *t*, the value of k is remarkably constant. It is true that N_1^2 does not vary greatly from 1, hence the constancy of k does not indicate at all certainly that the system is to be described by Equation 8 rather than Equation 9. It is even conceivable that the constancy of k is only apparent, due to a canceling of a variation with temperature and a more complex variation with N_1. That this should be the case in so many systems is, however, very improbable, or is, at any rate, an effect of a higher order, not seriously interfering with the practical value of the simpler Equation 8. Moreover, we shall see evidence later in which N_1 undergoes large variations with but little effect on k.

There appears to be a slight increase in k with increasing temperature for xylene, and a slight decrease for benzene. This is borne out by the fact that the critical mixing temperature with benzene is lower than that with xylene, indicating a crossing of the solubility curves at higher temperatures. It is noteworthy that this is in harmony with the correction for volume change given in Equation 3. The volume of liquid sulfur at 20" is 135 cc. (extrapolated), while the partial molal volumes of sulfur in the solvents benzene, toluene and xylene at 25° are, respectively, 138.7 cc., 133.4 cc. and 123.6 cc., indicating an expansion in forming the benzene solution and a contraction for the xylene solution.

Further evidence is furnished by the solubility data for violet solutions of iodine, which are taken from a paper by Hildebrand and Jenks.[11] Table II gives, as in Table I, the values of k for a series of temperatures. As in the previous table, k shows a very satisfactory constancy. In the case of carbon disulfide, the variation in N_1 is sufficient to make a considerable difference between N_1^2 and N_1^3, which are 0.83 and 0.75, respectively, at the highest concentration, showing that the equation with N_1^2 only suffices. It is interesting to state two further facts. The first is that the value of k for carbon disulfide falls to 181 at −20° and to 106 at −63°, but in this region the solution becomes brown and is no longer regular. Arsenic trichloride, which likewise gives brown solutions, behaves similarly, giving for k, 337 at 96°, 112 at 15° and 93 at 0°. The second fact is that while k remains constant for carbon disulfide solutions between 0 and 40°, there is a slight falling off for both heptane and carbon tetrachloride. It is possible, however, to correlate this behavior with the effect of volume changes mentioned earlier. From measurements of the density of these solutions made by Dawson,[12] we have calculated the partial molal volumes of liquid iodine in heptane, carbon tetrachloride and carbon disulfide to be, respectively, 63.9, 65.8 and 61.1 cc., which may be compared with the volume of 58.5 cc. for the extrapolated molal volume of liquid iodine.

TABLE II

SOLUTIONS OR IODINE—VALUES OR k

t	−63	−20	0	18	25	30	35	40	50
In C_7H_{16}	...	...	457	...	452	...	448	...	443
In CCl_4	...	...	395	...	386	...	389	...	384
In $CHCl_3$	...	...	302	298	...	299	...	...	...
In CS_2	(106)	(181)	188	...	190	192	...	191	...

Solubilities of naphthalene have been determined by Ward[13] over a wide temperature range. Table III gives random selections from his data for two non-polar solvents, hexane and carbon tetrachloride. Here

TABLE III

SOLUTIONS OF NAPHTHALENE

In Hexane

t	8.7	27.7	45.8	58.4	64.6	Mean k
$100N_2$	6.20	13.18	28.7	50.8	66.0	
k	158	155	149	152	146	152

In Carbon Tetrachloride

t	0.4	13.0	19.5	28.2	39.5	64.8	
$100N_2$	11.95	17.8	21.7	28.2	38.9	73.1	
k	35	37	37	38	35	37	37

---

[11] Hildebrand and Jenks, THIS JOURNAL, 42, 2180 (1920); *cf.*, also, ref. 2b, p 148

[12] Dawson, J. *Chem. Soc.*, **97,** 1046 (1910).

[13] Ward, J. *Phys. Chem.*, 30, 1316 (1926).

the concentrations of naphthalene become very high, so that the use of a cN_1^3 term would lead to very different results.

The data for stannic iodide obtained by Dorfman and Hildebrand[14] offer further opportunity for testing the equation. Unfortunately, we have no direct value for the heat of fusion of stannic iodide wherewith to calculate the ideal solubility; however, we have two ways of making reasonably good estimates. The first is to assume that all tetrahalides of this type will have about the same entropy of fusion. Table IV gives values of the melting points, T_m and heats of fusion, ΔH_m for several such halides, together with their quotient, the entropy of fusion. The values for ΔH_m are from Latimer,[15] except the last, which is from Tolloczko.[16]

TABLE IV

CONSTANTS OF HALIDES

	T_m	ΔH_m	$\Delta H_m/T_m$
Silicon tetrachloride	203.3	1845	9.08
Titanium tetrachloride	248	2233	9.00
Stannic chloride	240	2188	9.11
Stannic bromide	303	2750	9.08
		Mean	9.07

If we assume that $\Delta H_m/T_m$ for stannic iodide is also about 9.07, then, since T_m is 416.5, ΔH_m = 3775. Another estimate may be made by assuming that stannic iodide forms a nearly ideal solution with carbon disulfide, the evidence for which is given in the paper by Dorfman and Hildebrand. The slope of this solubility curve gives ΔH_m = 3940. We shall select in round numbers 3850. Calculating the ideal solubilities from this value, Equation 12 gives the values of k shown in Table V, omitting the figures for mole per cent.

TABLE V

VALUES OF k FOR SOLUTIONS OF STANNIC IODIDE

t, °C.	C_7H_{16}	CCl_4	$CHCl_3$	C_6H_6	$C_6H_4(CH_3)_2$	$C_2H_4Br_2$
10	434	315	305	268	249	177
25	436	317	298	267	249	174
40	440	313	296	261	246	171

It is interesting to note the form of the curve given by Equation 12 in Fig. 1, for several systems, using the mean values of k given in Table V. It can be seen that while the curves are nearly linear for small values of k, illustrated by ethylene bromide, as k becomes larger the curves take on the reversed S-shape noted particularly by Mortimer.[3] Furthermore, as the value of k becomes still larger, as in the case of heptane, there appear three values of log N_2 for a single temperature, two of which are stable

---

[14] Dorfman and Hildebrand, THIS JOURNAL, 49, 729 (1927).

[15] Latimer, THIS JOURNAL, 44, 90 (1922).

[16] Tolloczko, Chem. *Zentr.*, 1901, I, 989.

corresponding to the appearance of a second liquid phase, all three phases, containing stannic iodide at the same activity. Above this triple point the solid disappears and we are in the region of two liquid phases. The equation thus accounts for the type of system previously encountered with sulfur.[10] This portion of the system will be discussed in the following section. Illustrations similar to the above might be multiplied almost indefinitely, but that is hardly necessary.

Two-Phase Liquid Systems.—Equations 8, 9 and 10 invite application to systems of incompletely miscible liquids, as has been done by Heitler. Part of this section parallels his work, but this is done for the sake of completeness. We have as the condition of equilibrium that the activity of each component is the same in both phases, that is, $a_1' = a_1''$ and $a_2' = a_2''$, where the primes distinguish the two phases. Equation 9 then gives

$$\ln a_2' = \ln N_2' + \frac{b}{RT} N_1'^2 = \ln a_2'' + \ln N_2'' + \frac{b}{RT} N_1''^2$$

from which, since $N_{1'} + N_{2'} = 1$, and $N_{1''} + N_{2''} = 1$, we get

$$\ln \frac{1 - N_1'}{1 - N_1''} = \frac{b}{RT} (N_1''^2 - N_1'^2)$$

Equation 9 for component 2 is identical except for the exchange of subscripts. The two equations are simultaneous when $\frac{1 - N_1'}{1 - N_1''} = \frac{1 - N_2'}{1 - N_2''} = \frac{N_1'}{N_1''}$, when $N_1'' = N_2' = 1 - N_1'$. Substituting this in the above gives

$$\ln \frac{1 - N_1'}{N_1'} = \frac{b}{RT} (1 - 2N_1') \tag{13}$$

which can be used for calculating the composition of the liquid phases when b is known, or ***vice versa.*** The former calculation, unfortunately, requires the method of successive approximations, so it is best to calculate T from given values of b and N. This equation becomes indeterminate at the critical mixing temperature, T_c, so that it is best to relate T_c to N in the following way.

At the critical mixing point, we have the conditions that[17] $\left(\frac{\partial a}{\partial N}\right)_T = 0$ and $\left(\frac{\partial^2 a}{\partial N^2}\right)_T = 0$. Applying these to Equation 8 gives $RT_c = 2bN_1N_2$, and $N_1 = N_2 = 0.5$, whence

$$2RT_c = b \text{ or } T_c = 1.15\text{ k} \tag{14}$$

The same methods can be applied to the unsymmetrical Equation 9, giving, in place of Equation 13, two simultaneous equations requiring a graphic solution, and in place of Equation 14 two equations giving b and c in terms of T_c and the critical composition, from which calculation can be made in either direction. The discussion will be confined, however, to the simpler symmetrical case given by Equations 13 and 14.

---

[17] **Ref. 2b, p. 55.**

The solubility of stannic iodide in heptane between 10 and 40° gives $k = 437$. If we assume that there is no entropy of expansion and that k remains constant to the region of two liquid phases, above about 125°, we would have from Equation 13 the liquid solubility curve shown in Fig. 1, with a critical mixing temperature of 230°, instead of the experimentally determined value of 137°.[18] This discrepancy would be reduced somewhat, 10°, by the use of the unsymmetrical equation, and the uncertainty regarding the heat of fusion of stannic iodide permits of some variation between the two figures. We have noted, however, some tendency of k to diminish with rising temperature, and have seen in Equation 3 a reason why it should. It is evident, therefore, that an extrapolation of over 100° from solid solubility to critical mixing temperature would be extraordinarily sensitive to slight changes in k. If we calculate k from the critical mixing temperature by Equation 14, we get 356, while around 25° we found 437. The drift may be expressed by using $k = 643 - 0.7T$. If we use 356 as constant to calculate the liquid solubility curve, it is especially significant that, although this gives the correct critical temperature, the descending branches are too near together, while if we use the slightly variable k, the spread of the curve is nearly satisfactory, bringing the liquid and solid curves into approximate agreement. The values of k in Table V indicate that instead of the variation being linear with T, a more rapid variation exists; this would satisfy also the experimental points for the liquid–liquid system.

Mr. A. Wachter, at the author's request, has made a determination of the solubility of stannic iodide in iso-octane (2,2,4-trimethylpentane) at 25°, getting for the mole per cent. of stannic iodide 0.3399 and 0.3441, mean 0.342. This gives a value of k of 503. The critical solution temperature for the two liquid phase system is 195°, from which we can calculate k from Equation 14 to be 407. If the change of k with T is assumed to be linear, we can write $k = 671 - 0.565T$, which very nearly accounts for the experimental points, although here again a slightly more rapid variation with T would be required to give perfect agreement.

Sulfur solubility curves suggest an application of these same equations and a number of calculations have been made with results agreeing about as well as with stannic iodide. They are not here reproduced, however, since the presence of S_μ in the liquid adds a considerable complication.

The E.m.f. of Concentration Cells.—The measurements made in this Laboratory by Taylor[19] on the e.m.f. of molten alloy concentration cells and their temperature coefficients offer a peculiarly direct check on the existence of regular solutions of the sort conforming to our definition. A cell consisting of a pure metal and its alloy with a nobler metal, as

---

[18] Dice and Hildebrand, THIS JOURNAL, 50, *3023 (1928).*

[19] *N. W.* Taylor, THIS JOURNAL, *45,2865 (1923); cf.* also ref. 2b, Chap. XVI.

electrodes, separated by an electrolyte containing the ion of the baser metal, has an e.m.f. given by the equation

$$\mathrm{E} = \frac{RT}{\mathrm{NF}} \ln a_2 \tag{15}$$

Combining this with Equation 9 gives

$$\mathrm{E} = \frac{RT}{\mathrm{NF}} \ln \mathrm{N}_2 + b\mathrm{N}_1^2 + c\mathrm{N}_1^3 + \ldots\ldots \tag{16}$$

The temperature coefficient of the cell is then

$$\frac{\mathrm{dE}}{\mathrm{d}T} = \frac{R}{\mathrm{NF}} \ln \mathrm{N}_2 \tag{17}$$

that is, the temperature coefficient is the same as for an ideal solution of the same composition. That various alloys obey this relation remarkably well is shown in Table VI. This is all the more striking because only the first alloy conforms to Equation 8, the other two requiring the more complicated Equation 9. What difference there is is in the direction expected, that is, the observed values are greater.

TABLE VI

TEMPERATURE COEFFICIENTS OR E.M.P. OR ALLOY CONCENTRATION CELLS, IN MILLIVOLTS PER DEGREE

	Alloy, *Cd-Sn*			
Mole per cent. of Cd	8.3.5	25.8	56.9	63 0
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (obs.)	0.0113	0.067	0.030	0.026
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (calcd.)	.0107	.058	.025	.020
	Alloy, Cd-Pb			
Mole *per cent.* of Cd	12.3	26.9	50.9	
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (obs.)	0.095	0.063	0.036	
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (calcd.)	.090	.057	.026	
	Alloy, Zn-Cd			
Mole *per cent.* of Zn	15.0	25.1	34.4	69.1
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (obs.)	0.079	0.061	0.047	0.016
$\frac{\mathrm{dE}}{\mathrm{d}T}$ (calcd.)	.082	.060	.046	.016

Not all such solutions are regular. The alloys of zinc and tin, and also of cadmium and bismuth, investigated by the same author, are irregular. This is not surprising in view of the departure of each, especially the latter, from the usual type of relation between log (a/N) and N.

Other Relations. 1. The Heat of Solution.—When the temperature of a saturated solution of X_2 is changed, saturation is maintained by having the change in fugacity of the solid phase, with the temperature only, equal to the change in fugacity of the same substance in solution, due to changes in both temperature and composition. Formally expressed this gives

$$\mathrm{d} \ln f_2^s = \mathrm{d} \ln f_2 = \left(\frac{\partial \ln f_2}{\partial T}\right)_{\mathrm{N}} \mathrm{d}T + \left(\frac{\partial \ln f_2}{\partial \ln \mathrm{N}_2}\right)_T \mathrm{d} \ln \mathrm{N}_2$$

But

$$\frac{d \ln f_2^s}{dT} = \frac{H_2^* - H_2^s}{RT^2} \text{ and } \frac{\ln f_2}{T} = \frac{H_2^* - \bar{H}_2}{RT^2}$$

where H_2^* and H_2^s are the heat contents of the vapor and solid, respectively, and $\bar{H}_2$ is the partial molal heat of solution; we can write, therefore

$$\frac{\bar{H}_2 - H_2^s}{RT^2} = \left(\frac{\partial \ln f_2}{\partial \ln N_2}\right)_T \frac{d \ln N_2}{dT} \tag{18}$$

For regular solutions, the partial differential can be obtained from Equations 8 or 9. Using the latter, and remembering that $f_2/f_2^\circ = a_2$, where f_2° is the fugacity of the pure liquid, we get

$$\left(\frac{\partial \ln f_2}{\partial \ln N_2}\right)_T = 1 - \frac{2b\, N_1N_2}{RT} \tag{19}$$

where $N_1 + N_2 = 1$. This equation expresses the deviation of a system from either Henry's law, $f_2 = lN_2$, where l is a constant, or from Raoult's law, where the constant becomes f_2°. It occurs frequently in the derivations of thermodynamic equations. It should be noted that $(\partial \ln f_2/\partial \ln N_2)_T$ approaches unity, first, when b approaches zero, that is, when Raoult's law is obeyed throughout the entire range of composition; second, when either N_1 or N_2 approaches zero, that is, when the solution is very dilute in either component. Only under these conditions, therefore, does the slope of the solubility curve, log N_2 *vs.* $1/T$, give directly the heat of solution. The equation for the heat of solution results from the substitution of Equation 19 in 18, giving

$$\frac{\bar{H}_2 - H_2^s}{RT} = \left(1 - \frac{2bN_1N_2}{RT}\right) \frac{d \ln N_2}{dT} \tag{20}$$

In view of the form of the curve for large deviations from ideal shown in Fig. 1, it is evident, as stated earlier, that a straight line drawn through the melting point gives a very erroneous value for the heat of solution. On the other hand, the tangent to the curve when log N is small gives the heat of solution rather accurately.

2. The Heat of Mixing.—In deriving Equation 8, the assumption was made that the heat of mixing is given by an equation such as 7. It may, of course, prove necessary in dealing accurately with some regular systems to add higher powers of N. Data upon heats of mixing are very meager, but the evidence is favorable for the approximate equality of free energy and heat of mixing. Taylor[19] pointed this out in connection with his measurements, and more recently Butler[20] has given a more quantitative calculation based upon these same measurements.

It is noteworthy that Equation 16 becomes equivalent to the well known Cady[21] equation, in view of the identification of the terms $bN_1^2 + cN_1^3 + \ldots$

---

[20] Butler, THIS JOURNAL, **47,** 117 (1925).

[21] Cady, *J. phys. Chem.,* 2,551 (1898).

with the heat effect. The failure of this equation to give a more complete agreement with the experimental data we attribute to its application to irregular systems, and to the use of concentration instead of mole fraction to express composition.

3. Volume Change on Mixing.—Differentiating Equation 8 with respect to the pressure, P, upon the liquid phase at constant N and T gives

$$\left(\frac{\partial \ln a_2}{\partial P}\right)_{\text{N,T}} = \frac{\text{N}_1^2}{RT}\frac{db}{dP}$$

(the second differential is not written as a partial since b is practically independent of N and T) but this is equal[22] also to $(\bar{\text{v}}_2 - \text{v}_2)/RT$, where v_2 is the molal volume and $\bar{\text{v}}_2$ the partial molal volume. We therefore write

$$\bar{\text{v}}_2 - \text{v}_2 = \text{N}_1^2\frac{db}{dP} \tag{21}$$

This harmonizes with a relation discovered by Biron[23] that the expansion of two liquids upon mixing to form a mole of mixture is

$$\Delta V = (\bar{\text{v}}_1 - \text{v}_1)\text{N}_1 + (\bar{\text{v}}_2 - \text{v}_2)\text{N}_2 = K\text{N}_1\text{N}_2$$

where K is db/dP. It also gives justification for the relation discovered some years ago by the writer[24]

$$\ln\frac{a_2}{\text{N}_2} = K'(\bar{\text{v}}_2 - \text{v}_2)$$

where K' is an empirical constant. Comparing this with Equation 8 gives $K'(\bar{\text{v}}_2 - \text{v}_2) = b\text{N}_1^2$. Combining with Equation 21 gives $K'\text{N}_1^2(db/dP) = b\text{N}_1^2$ or $(d \ln b/dP) = (1/K)$, that is, K' is a constant for a given system calculable from b and its change with pressure.

4. The Gibbs adsorption equation is

$$\left(\frac{\partial\gamma}{\partial \ln f_2}\right) = -u_2RT \tag{22}$$

where γ is the surface tension of a solution, and u_2 the amount of adsorbed solute per cm.^{2} of surface. The partial differential signifies constant surface. We may write the mathematical identity

$$\left(\frac{\partial\gamma}{\partial \ln \text{N}_2}\right) = \left(\frac{\partial\gamma}{\partial \ln f_2}\right)\left(\frac{\partial \ln f_2}{\partial \ln \text{N}_2}\right)$$

The first differential on the right is given by Equation 22, and the second by Equation 19, giving

$$\frac{\partial\gamma}{\partial \ln \text{N}_2} = -u_2RT\left(1 - \frac{b\text{N}_1\text{N}_2}{RT}\right) \tag{23}$$

This equation is usually written with the concentration in place of the mole fraction and without the term in parenthesis. The omission of this correcting term may be serious, for it is those solutions which deviate

---

[22] Ref. 2b, p. 61.

[23] Biron, *J. Russ. Phys.-Chem. Soc.*, **44**, 1264 (1912).

[24] *Cf.* ref. 2b, pp. 61–65.

most strongly from Raoult's law (that is, which show a large value for *b)* that show large adsorption. Of course this is compensated by the fact that when the solution is very dilute, $N_2 = 0$, and the correcting factor approaches unity. The usual neglect of the deviation from the ideal solution is undoubtedly partly responsible for the lack of agreement often found when testing the Gibbs equation in the simplified form. Equation 23 offers a simple means for making the correction for regular solutions.

Evaluation of the Constant.—The application of the various equations given in this paper requires, of course, the evaluation of the constant b, or, when necessary, additional constants in Equation 9. The numerous solubility data already discussed by the author show clearly that the deviations from ideality, now expressed by the magnitude of b or k, are rather closely determined by the difference in internal pressure of the two components. There is evidence, however, that this is not the only factor and efforts are being made to formulate the exact relation between b and internal pressure. This study demands certain experimental data that we are now endeavoring to secure, after which it is hoped that a report upon the subject may be made.

Meanwhile, it would be possible to give an improved substitute for Mortimer's table of solubility "factors" by constructing a table of internal pressure functions that would give values of k by difference. This is too long a task for inclusion with this paper, but anyone confronted with problems involving regular solutions may make rather good estimates of the constant upon an additive basis by the aid of existing data involving other systems. Again, where a single experimental point involving the activity of a system is at hand, its general behavior can be calculated.

In plotting activity data, it has been pointed out[25] that log (a_2/N_2) (or log γ_2, where γ_2 is the activity coefficient), when plotted against mole fraction, gives a simple expression for deviations from ideality. It is becoming rather general practice, even with aqueous solutions, which are far from regular, to plot log γ. The present treatment suggests that where temperature changes are involved the most advantageous function to plot would be T log γ_2 against N_1^2.

Summary

1. Certain solutions of a common solute in various solvents which give families of solubility curves, and from which chemical effects and association changes are absent, are designated as regular solutions. They are defined as solutions in which no change in entropy, except for the small entropy of expansion, is involved in the transfer of a constituent from it to an ideal solution of the same concentration.

2. An equation given by van Laar upon the basis of the van der Waals

---

[25] Ref. 2b, Chap. V.

equation of state, and recently derived by Heitler upon different assumptions, is applied to a large number of solutions with very satisfactory results.

3. The equation is applied to the calculation of other properties dependent upon activity, including the e.m.f. of concentration cells, the heat of solution of solids, the expansion on mixing and the Gibbs adsorption equation.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VIII. THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID BOTH IN THE PRESENCE AND ABSENCE OF URANYL SULFATE

BY WILLIS CONWAY PIERCE, A. LEVITON AND W. ALBERT NOYES, JR.

RECEIVED JULY 24, 1928 PUBLISHED JANUARY 8, 1929

The photochemical decompositions of many organic acids have been studied in some detail. Of these none has received more attention than the decomposition of oxalic acid. It is not necessary, at the present time, to summarize all of the work that has been done.[1] Earlier work on the nature of the products formed has been shown by Allmand and Reeve[2] not to agree with the composition of the products formed during the early stages of the reaction. These authors show that the principal reaction consists in the formation of formic acid and carbon dioxide. Since the former may be decomposed photochemically, other products would result with long exposures. They found, further, that the quantum efficiency varied with wave length, the highest value obtained being 1/100 at 265 $m\mu$. Anderson and Robinson[3] report an average yield of 1/1392 molecule per quantum for radiation from a quartz mercury arc lamp.

The photochemical decomposition of oxalic acid sensitized by uranyl salts has also received considerable attention. Measurements of quantum efficiency of the sensitized reaction are somewhat at variance, but the best evidence indicates that the value is approximately one.[4,5] Büchi,[4] from a consideration of his determinations of the rate of photochemical decomposition of oxalic acid in solutions of varying concentration and with various amounts of uranyl sulfate, has come to the conclusion that a complex molecule, or a molecule of uranyl oxalate, is the photosensitive mole-

Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 146,229, has given a partial summary of recent work on this reaction.

[2] Allmand and Reeve. J. *Chem.* Soc., **129**, 2834 (1926).

[3] Anderson and Robinson, THIS JOURNAL, **47**, 718 (1925).

[4] Büchi, Z. *physik. Chem.*, **111**, 269 (1924).

[5] Bowen and Watts, J. *Chem. Soc.*, **127**, 1607 (1925).

cule in the reacting system. He further supports this conclusion by the data of Henri and Landau,[6] which show that the absorption coefficients of oxalic acid and uranyl salts are not additive in solutions containing both substances, but that a marked increase in the absorption of uranyl sulfate solutions is brought about by the addition of small amounts of oxalic acid. As pointed out by Kistiakowsky,[1] there is further evidence in favor of the sensitivity of the complex in the comparison of the quantum efficiencies with and without catalyst.

Corresponding work on other acids has been attempted, Thus Müller[7] has found that approximately one molecule of lactic acid was decomposed per quantum absorbed in the presence of uranyl sulfate. Bolin[8] found, however, that uranyl salts in the presence of lactic acid are quantitatively reduced. The rate of reaction reached a steady value with increase in concentration of uranyl sulfate. No evidence for or against complex formation is contained in either of these papers.

Some work has been done on the photochemical decomposition of malonic acid. Fay[9] in the presence of catalyst, found that the rate of decomposition in sunlight was exceedingly slow. Kailan[10] found that more carboxyl groups were decomposed in the case of malonic acid than in the case of oxalic acid when the two were exposed to full radiation from a quartz mercury arc lamp. Berthelot and Gaudechon[11] found that uranyl salts acted as catalysts in the photochemical decomposition of malonic acid. Volmar[12] states that the main products of the photochemical decomposition of malonic acid are acetic acid and carbon dioxide.

The present work was undertaken with the object of determining the possible mechanisms of the action of uranyl sulfate in catalyzing the photochemical decomposition of malonic acid.

I. Experimental Procedure and Results

In all of the work which follows the amount of decomposition of malonic acid was determined by titration with sodium hydroxide solutions (free from carbonate) with the use of phenolphthalein as the indicator. The solutions were boiled to remove carbon dioxide. In solutions containing uranyl sulfate (below 0.01 M), the uranyl sulfate titrated toward phenolphthalein as though it were an equivalent amount of sulfuric acid. This point was repeatedly checked by making up solutions containing a known weight per unit volume of $UO_2SO_4 \cdot 3H_2O$. The amount of decomposition

---

[6] Henri and Landau, *Compt. rend.*, 158, 181 (1913).

[7] Mullcr, *Biochem.* Z., 178, *77* (1926).

[8] Bolin, Z. *physik. Chem.*, 87,490 (1914).

[9] Fay, *Am. Chem.* J., 18,269 (1896).

[10] Kailan, *Monatsh.*, 34, 1209 (1913).

[11] Berthelot and Gaudcchon, *Compt. rend.*, 157,333 (1923).

[12] Volmar, *Compt. rend.*, 180, 1172 (1925).

agreed roughly with that determined by gas evolution, but the latter method of measurement was not considered to be as accurate as the titration method.

(a) Analysis of the Gas Evolved during Decomposition.—A solution of malonic acid was placed in a quartz reaction vessel sealed to a Toepler pump by means of a graded seal. The solution was outgassed as thoroughly as possible and then exposed to the full radiation from a quartz mercury arc lamp. The evolved gases were pumped off and collected in a small test-tube over mercury. The gases were then analyzed by the micro method of Reeve.[13] The total volume was measured in a capillary tube. The gas was swept into the test-tube again and a small piece of fused potassium hydroxide introduced to absorb the carbon dioxide. The residual gas was measured in the capillary tube. An attempt was made to analyze the residual gas by sparking with air, but no contraction (beyond experimental error) was noticed. After sparking the gas was again tested for carbon dioxide but no further absorption was found. Sparking alone, without admixture of air, did not produce any consistent change in volume. This probably indicates that no appreciable quantity of methane or carbon monoxide is formed. Table I presents the results obtained. The residue seems to be largely air.

TABLE I

ANALYSIS OF THE GAS FORMED DURING PHOTOCHEMICAL DECOMPOSITION OR MALONIC ACID

Concn. of malonic acid, 0.05 M. 1 cm. = 0.0227 cc.

Conditions	Total gas, cm.	Residue, cm.	CO_2 by vol., %
No catalyst	12.6	0.7	94.5
No catalyst	10.0	.4	96.0
No catalyst	16.2	.7	95.7
No catalyst	18.6	.75	96.0
Catalyst 0.005 M	54.5	2.3	96.0
Same (Pyrex vessel)	80.0	0.4	99.5

It is probable that the difference between the last analysis and the others is due to more thorough outgassing in the Pyrex vessel.

We feel safe in stating that the early stages of malonic acid decomposition lead almost exclusively to the formation of carbon dioxide and acetic acid. This seems to be true both in the presence and absence of catalyst and in the presence of catalyst whether the full mercury arc spectrum is used or just those wave lengths longer than 300 mμ.

(b) Effect of Uranyl Sulfate on the Rate of Photochemical Decomposition with Radiation from the Full Mercury Arc.—A series of decompositions was carried out in which solutions 0.05 M with respect to malonic acid and containing various concentrations of uranyl sulfate were exposed to radiation from the full mercury arc in a vessel open to the air. It was shown that the rate was practically the same in the absence of air by carrying out a few experiments in a closed vessel evacuated to the vapor pressure of water over the solution. The determinations were made by titration (see above). Table II (see also Fig. 1) shows the relative rate of decomposition with varying concentration of catalyst. The values are averages of three determinations.

(c) The Determination of the Quantum Efficiency.—The light intensities were all measured by means of a thermopile calibrated by a standard source of radiation

---

[13] Reeve, J. *Chem. Soc.*, 125, 1946 (1924).

TABLE II

EFFECT OF CATALYST ON THE REACTION RATE

Concn. of UO_2SO_4 (*M*)		0.0000	0.0002	0.0005	0.0010	0.0025	0.005	0.010
Rel. reac. rate		.33	.58	.62	.85	1.02	1.01	.97
Rel. rate calcd. by eq. (1)		.33	.50	.68	.85	0.98	1.00	1.00
Rel. rate calcd. by eq. (2)	I	.33	.52	.68	.88	1.04	1.01	0.84
	II	.33	.55	.65	.85	1.06	1.01	.73

furnished by the Bureau of Standards; 1 cm. deflection corresponded to 2.0 ergs per mm.^{2} per second.

The percentage absorption was determined by a modification of the procedure used by Herr and Noyes.[14] A perforated plate was placed in front of a quartz mercury arc lamp. The radiation was made into a slightly diverging beam by means of a quartz lens and then passed through a water cell about 3.2 cm. in thickness. The absorption cell containing water was then fixed in such a way that it could be interposed between the water cell and the thermopile. After the decrease in deflection due to interposition of the cell filled with water had been determined, the cell was filled with the solution to be studied and the decrease in deflection again determined. The difference between the two percentage decreases was taken as the percentage of the radiation absorbed by the solution.

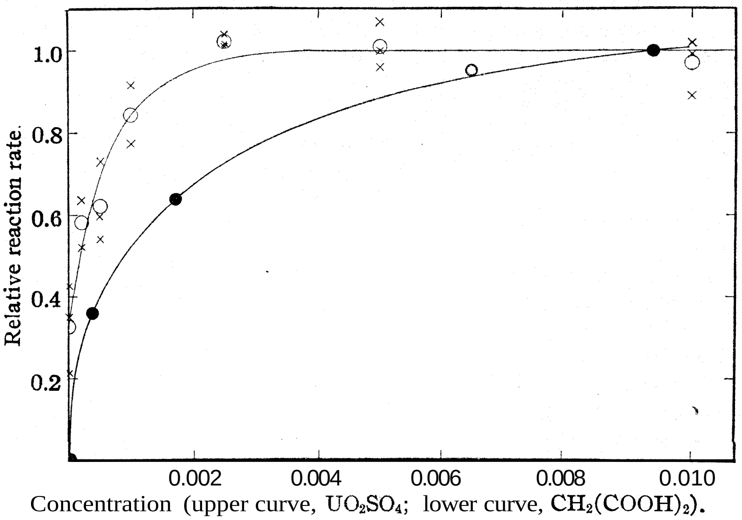


Fig. 1.—Upper curve is that of Equation 1. Crosses are observed values, circles are average values. The concentration of $CH_2(COOH)_2$, is 0.05 M. Through quartz. The lower curve shows the variation in rate with concentration of malonic acid (see Table VII). Concentration of UO_2SO_4 is 0.01 M. Through Pyrex glass.

The actual determination of the amount of decomposition required a more intense radiation than could be obtained by the system described in the preceding paragraph. The radiation was passed (without a lens) through an opening about two centimeters in diameter, through the water cell and then through the solution to be studied. The

---

[14] Herr and Noyes, THIS JOURNAL, 50, 2345 (1928).

intensity of the incident radiation was obtained by placing the thermopile in the position to be occupied by the reaction vessel. The value of the incident intensity and the percentage absorption together with the amount of decomposition permitted a calculation of the quantum efficiency, providing the average wave length of the radiation were determined. From a consideration of the absorption coefficients of malonic acid as determined by Bielecki and Henri[15] and the distribution of the intensity of the radiation from the mercury arc given by Reeve,[16] the average wave length was calculated to be 250 mμ in the absence of catalyst. In the presence of catalyst, absorption was assumed to be complete for lines below 320 mμ and the average wave length was calculated to be 290 mp. Both of these values should be good to about 10 mp, although it is recognized that the intensity distribution given by Reeve would probably not imply high accuracy to the lamp used in these experiments. That they were in approximate agreement was ascertained by the use of a monochromatic illuminator with the thermopile. For radiation transmitted by Pyrex, the average wave length absorbed in the presence of catalyst was taken as 320 mp. The absorption of the Pyrex plate used was determined with a spectrograph and rotating sector. Log $I/I_0 = -0.5$ at 313 mμ and -1.2 at 301 mp. Thus very little radiation below 300 mμ was transmitted. The following tables show the data obtained.

TABLE III

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID WITHOUT CATALYST

(Concn., 0.05 M)

Duration of run, hours	5.4	6.67	7.25
Fraction absorbed	0.031	0.031	0.031
Ergs. absorbed × 10^{-8}	4.225	5.98	1.78
Amt. decomposed (cc. of NaOH)	1.49	1.80	0.55
Normality of NaOH	0.0481	0.0481	.0481
Molecules decomp. X 10^{-19}	4.35	5.24	1.60
Molecules per erg X 10^{-11}	1.03	0.876	0.899
Average wave length, mμ	250	250	250
Quantum efficiency	0.81	0.68	0.71 av. 0.73

(Since the fraction 0.031 is the difference between 0.110 ± 0.005 and 0.141 ± 0.005, the average quantum efficiency is 0.73 ± 0.25.)

TABLE IV

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID WITH CATALYST

Malonic acid, 0.05 M. Uranyl sulfate, 0.005 M

Duration of run, hours	5.3	3.5	3.5
Fraction absorbed	0.276	0.276	0.276
Ergs. absorbed × 10^{-8}	38.4	24.9	23.8
Amt. decomposed (cc. of NaOH)	5.35	5.05	4.45
Normality of NaOH	0.0481	0.0327	0.0327
Molecules decomposed X 10^{-19}	15.57	10.0	8 81
Molecules per erg X 10^{-11}	0.416	0.402	0.370
Average wave length, mp	290	290	290
Quantum efficiency	0.28	0.27	0.25 av. 0 27

The fraction 0.276 should be accurate to ±0.02. The quantum efficiency is 0.27 ± 0.02.

---

[15] Bielecki and Henri, *Ber.*, 45, 2819 (1912).

[16] Reeve, J. Phys. *Chem.*, 29, 34 (1925).

Table V

The Quantum Efficiency of the Photochemical Decomposition of Malonic Acid with Catalyst and a Pyrex Filter Interposed

Malonic acid, 0.05 M. Uranyl sulfate, 0.005 M

Duration of run, hours	7.3	6.0	4.0	
Fraction absorbed	0.160	0.112	0.112	
Ergs. absorbed × 10^{-8}	20.5	9.26	8.66	
Amt. decomposed (cc. of NaOH)	4.05	1.92	1.83	
Normality of NaOH	0.0327	0.0327	0.0327	
Molecules decomp. × 10^{-19}	8.02	3.80	5.82	
Molecules per erg × 10^{-11}	0.390	0.411	0.442	
Average wave length, $m\mu$	320	320	320	
Quantum efficiency	0.24	0.25	0.27	av. 0.25

The fractions absorbed should be accurate to ±0.02. The average quantum efficiency is 0.25 ± 0.04.

Since the thermopile was calibrated for relatively feeble light intensities and used for high light intensities in the above experiments, the question might arise as to the validity of the light intensity measurements. To test this point a 1000-watt lamp was used and the inverse square law assumed. It was found that within the accuracy of the application of the inverse square law, the measurements of the high light intensities by the thermopile were justified.

(d) Determination of Absorption Coefficients.—It has already been pointed out that Henri and Landau[6] have shown that the addition of small amounts of oxalic acid to uranyl sulfate causes a marked increase in the absorption coefficients. This is, in general, good evidence for the formation of a complex. Similar experiments were carried out with malonic acid using a rotating sector in conjunction with a spectrograph. Absorption coefficients for the uranyl sulfate alone were in approximate agreement (although slightly higher) with those of Henri and Landau. Addition of malonic acid did not produce a change greater than the experimental error. A solution containing both malonic acid and uranyl sulfate showed nearly the same absorption as a solution of malonic acid placed in series with a solution of uranyl sulfate in such a manner that the total number of molecules traversed by the radiation was the same. We find, therefore, no evidence for or against complex formation from this source.

(e) Effect of the Addition of Sulfuric Acid.—Two solutions, each 0.05 M with respect to malonic acid, to one of which was added 0.005 M sulfuric acid, were exposed under identical conditions to radiation from a quartz mercury arc lamp. The amounts of decomposition were identical within about 2%.

(f) Effect of Variation of the Malonic Acid Concentration with Constant Concentration of Uranyl Sulfate.--Six test-tubes (Pyrex) were filled with ten cc. each of solutions made up to 0.01 M with respect to uranyl sulfate and with varying amounts of malonic acid. Three concentrations were used so that duplicates were made of each determination. In addition one tube was filled with a solution 0.01 M with respect to uranyl sulfate and 0.05 M with respect to oxalic acid. The tubes were rotated in regular order before a quartz mercury arc lamp (without water filter) so that each received the same extent of illumination. The oxalic acid (since it decomposed more rapidly than the malonic acid) and one solution of malonic acid were exposed for a shorter time than the others. Table VI shows the data for these two tubes which were titrated early.

As will be seen in Table VII, a similar solution with 0.1 *M* malonic acid decomposes 1.58 times as rapidly as 0.02 M malonic acid. If it is assumed that the light absorbed by the malonic acid-uranyl sulfate solution is the same as for the oxalic acid-uranyl

TABLE VI

COMPARISON OF RATE FOR OXALIC AND MALONIC ACIDS IN THE PRESENCE OF URANYL SULFATE

$KMnO_4$, 0.1050 N. NaOH, 0.0327 N. Solution I, 0.01 M UO_2SO_4, 0.05 M $H_2C_2O_4$. Solution II, 0.01 M UO_2SO_4, 0.02 M $HO_2CCH_2CO_2H$.

Solution I		Solution II	
Cc. $KMnO_4$ (blank).........	9.72	Cc. NaOH (blank).........	19.06
Cc. $KMnO_4$ (after exposure)..	5.25	Cc. NaOH (after exposure)..	18.00
Difference..................	4.47	Difference.................	1.06
Moles $H_2C_2O_4$ decomposed.....	0.000235	Moles malonic acid decomposed..................	0.0000347

sulfate solution and that the quantum efficiency for the decomposition of the latter is one,[4] the quantum efficiency for the decomposition of malonic acid (0.1 *M*) in the presence of uranyl sulfate 0.01 M is found to be 0.23, which is in good agreement with the values given in Table V.

Since the oxalic acid solution probably absorbs more than the malonic acid solution, this figure is too low rather than too high. Table VII shows the variation of rate of decomposition with concentration of malonic acid with constant concentration of uranyl sulfate.

TABLE VII

VARIATION OF RATE WITH CONCENTRATION OF MALONIC ACID

NaOH, 0.0327 *N*. Solutions all 0.01 M in UO_2SO_4. Solution III, 0.10 M in malonic acid, Solution IV, 0.02 M in malonic acid, Solution V, 0.005 *M* in malonic acid.

Solution	NaOH (blank), cc.	NaOH (after exposure), cc.	*Diff.* (av.)	Rel. rate
III	66.90	64.55		
	67.01	64.53	2.41	1.00
IV	19.06	17.53	1.53	0.64
	19.06			
V	10.24	9.35	0.86	0.36
	10.15	9.34		

(g) Effect of Pyrex on the Rate of Decomposition of **Malonic** Acid without Catalyst.—One experiment was carried out with a Pyrex filter in the absence of catalyst. Decomposition was observed at about one-sixth the rate without Pyrex. Attempts to measure the light absorption failed, however, as the amount of light absorbed by the solution was so slightly different from that absorbed by water. This may be taken to indicate that the quantum efficiency for the pure acid is not greatly variable with frequency.

II. Discussion of Results and Conclusions

We may summarize the results reported above as follows. 1. The decomposition of malonic acid, both with and without addition of uranyl sulfate, gives carbon dioxide and acetic acid.

2. The rate of decomposition in the presence of radiation from a mercury arc lamp increases with addition of uranyl sulfate and approaches a constant value. The average rates indicate a slight falling off when the concentration of uranyl sulfate exceeds about 0.005 M, but this falling off is smaller than the experimental error.

3. The quantum efficiency of the catalyzed reaction is smaller than for the uncatalyzed reaction,

4. With constant uranyl sulfate concentration, the rate of photochemical decomposition of malonic acid decreases with the decrease in malonic acid concentration. However, the rate is not proportional to the malonic acid concentration but varies approximately as the cube root of the latter.

5. There is no evidence which indicates a complex molecule, with the possible exception of the observation by Fay[9] that uranyl malonate is soluble in an excess of malonic acid.

6. In view of the fact that addition of sulfuric acid produces no marked change in rate of decomposition, the extent of ionization of the malonic acid does not make an appreciable difference.

7. The effect of wave length on the quantum efficiency is not marked.

It is of interest to ascertain what type of equation will satisfactorily reproduce the effect of uranyl sulfate on the reaction rate. Since the malonic acid concentration was kept constant during these runs, there is only one variable concentration to consider. In Table II are given values calculated by means of the following equation

$$-\mathrm{d}[\mathrm{H_2Ma}]/\mathrm{d}t = K_1I_0(1 - 10^{-kCl}) + K_210^{-kCl} \qquad (1)$$

where $[\mathrm{H_2Ma}]$ represents the concentration of malonic acid, C is the concentration of uranyl sulfate in millimoles per liter, l is the thickness of the solution (here kept constant), I_0 is the incident intensity, k is the absorption coefficient of the uranyl sulfate and K_1 and K_2 are constants. The values in Table II (see also Fig. 1) were obtained by using $K_1I_0 = 1.00$, $K_2 = 0.327$, $kl = 0.64$; l was about 2 cm. in these experiments, so that the absorption coefficient is rather high. However, monochromatic light was not used and the absorption coefficient of uranyl sulfate increases very rapidly below 330 mμ.[6]

Equation 1 may be derived by assuming that there are two independent reactions, one due to the light absorbed by the catalyst and the other due to the light absorbed by the malonic acid. The first term on the right-hand side of the equation would represent the rate of the former reaction and the second term the rate of the latter. $1-10^{-kCl}$ would represent the fraction of the light absorbed by the catalyst and 10^{-kCl} would represent the fraction unabsorbed. Of the latter a definite fraction would be absorbed by malonic acid since its concentration is maintained constant in all runs.

With the values chosen, Equation 1 shows that the relative reaction rate should approach unity asymptotically. The fact that such small concentrations of uranyl sulfate cause the relative rate to approach unity so rapidly means that the absorption coefficient is very high.

In Table II are also given values calculated by means of the following equation.

$$-\mathrm{d}[\mathrm{H_2Ma}]/\mathrm{d}t = \frac{K_1'I_0(1-10^{-kCl})}{1+K_3C}[\mathrm{H_2Ma}] + K_2I_0\,10^{-kCl} \qquad (2)$$

All terms have the same meaning as in Equation 1. For the values listed in the row marked I, the following constants were used: $K_1'I_0 = 12.9$, $kl = 0.0411$, $K_3 = 1.0$, $K_2 = 0.327$. For the row marked II, $K_1'I_0 = 3.97$, $kl = 0.1$, $K_3 = 0.402$, $K_2I_0 = 0.327$. This equation may be derived by assuming that a complex molecule is formed when an excited uranyl sulfate molecule (or uranyl ion) collides with a malonic acid molecule and that this complex may either decompose into the final products of the reaction (a first order reaction) or may be deactivated by collision with a uranyl sulfate molecule (or uranyl ion). The second term on the right-hand side of the equation has the same significance as the similar term in Equation 1.

Equation 1 agrees with the experimental values satisfactorily. Equation 2 is of such a nature that the rate passes through a maximum as C increases. It may be made to fit the data at lower concentrations as well as Equation 1, but the rate calculated by its use always falls off more rapidly than the experimental value beyond 0.005 M uranyl sulfate if a reasonably good fit is made for the lower part of the curve. We may conclude, therefore, that the assumption that with constant concentration of malonic acid the rate of the catalyzed reaction is proportional to the intensity of the light absorbed by the catalyst does not disagree with the experimental facts.

When attention is turned to the variation of rate with concentration of malonic acid, the question becomes somewhat more complicated. If the rate were independent of concentration of malonic acid, every activated uranyl sulfate molecule (or uranyl ion) would have a chance to react and the low quantum efficiency would be due to the low probability of reaction of the malonic acid after activation by a collision of the second kind. The variation of reaction rate with concentration indicates, however, that part of the absorbed radiation is ineffective in producing activation of malonic acid. This is also borne out by the low value of the quantum efficiency. Likewise complex formation does not offer a simple explanation of the results obtained. The most logical explanation is based on the assumption that uranyl sulfate is activated by absorption of the radiation and that it may lose its energy before encountering a malonic acid molecule. If the deactivation process is a first order reaction and the activation of the malonic acid proportional to the concentration of activated uranyl sulfate molecules and to the concentration of malonic acid, an equation of the following type is obtained

$$\textit{Rate} = KC'/(1 + kC) \qquad (3)$$

if the light absorbed remains constant. C' is the concentration of malonic acid. This equation does not satisfy the data completely.

One other possibility may be considered. If an activated uranyl sulfate molecule could be deactivated by a collision with another uranyl sulfate molecule or could activate a malonic acid molecule upon collision, the reaction rate should be proportional to the ratio $C'/(C' + C)$, where C' is the concentration of malonic acid and C the concentration of uranyl sulfate. Using average concentrations during each run, relative rates in Table VII may be calculated to be 1.00, 0.70 and 0.30 instead of 1.00, 0.64 and 0.36, respectively. This is a reasonably good check in view of the fact that the water may easily play a part in the deactivation process. It is to be noted that this simple explanation would also account for the slight decrease in rate with high concentrations of uranyl sulfate.

The decomposition of malonic acid in the presence of uranyl sulfate seems, therefore, to be of a type differing from that of oxalic acid. Complex formation seems to offer a reasonable explanation of the results obtained with the latter, although there may still be some doubt as to the quantum efficiencies (the quantum efficiencies in the absence of catalyst would seem to be too low). Most authors are in agreement that addition of uranyl sulfate to oxalic acid increases the quantum efficiency, while addition of uranyl sulfate to malonic acid causes a lowering. While no definite evidence has been obtained for the existence of a light-sensitive complex in solutions containing both uranyl sulfate and malonic acid, such an explanation has not been definitely eliminated. A complex, if present, must either be small in concentration compared to the amount of uranyl sulfate added or be relatively insensitive to the action of radiation.

Summary

1. Malonic acid, both in the presence and absence of uranyl sulfate, decomposes initially to give carbon dioxide and acetic acid.
2. The rate of decomposition in the presence of radiation from the mercury arc increases with addition of uranyl sulfate and approaches a constant value (although there may be a slight decrease at high concentrations).
3. The quantum efficiency of the catalyzed reaction is lower than for the uncatalyzed reaction at the concentrations studied.
4. With constant concentration of uranyl sulfate (0.01 M), the rate of decomposition decreases with decrease in concentration of malonic acid. Empirically, the rate is approximately proportional to the cube root of the malonic acid concentration.
5. No good evidence is obtained for the presence of a complex molecule which is light sensitive.
6. Various mechanisms of the reaction have been discussed.

CHICAGO, ILLINOIS

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

THE INHIBITIVE ACTION OF ALCOHOLS ON THE OXIDATION OF SODIUM SULFITE

BY HUBERT N. ALYEA[1] AND HANS L. J. BÄCKSTRÖM[2]

RECEIVED JULY 25, 1928 PUBLISHED JANUARY 8, 1929

In a previous paper by Backstrom[3] it was shown that the photochemical oxidation of a sodium sulfite solution is a chain reaction, and that those substances which are known to inhibit the thermal reaction[4] have a similar effect on the photochemical reaction. The results obtained with alcohols as inhibitors were particularly striking, showing a quantitative agreement between light and dark reaction. It must be assumed, therefore, that the thermal reaction also is a chain reaction, and that the role of the inhibitor, in the thermal as well as in the photochemical oxidation, consists in the breaking of reaction chains.

In a later paper,[5] Backstrom discussed the different ways in which the inhibitor might act in this process and concluded that the mechanism by which the chains are broken is probably an induced reaction between the inhibitor and one of the reactants. In the particular case of the alcohols this is indicated by Bigelow's[4a] results on the inhibitory power of the four butyl alcohols in the oxidation of sulfite solutions. He found that the primary, the secondary and the isobutyl alcohols all acted as inhibitors, but that the tertiary had no effect. Since the first three alcohols can be oxidized easily to aldehydes and ketones, whereas the tertiary can only be oxidized with the simultaneous destruction of the molecule, there seems to be a direct relation between inhibitory power and oxidizability in this case;[6] and the logical conclusion seems to be that the alcohols are actually oxidized in the process of breaking the reaction chains. Without postulating any special mechanism of chain propagation, we may describe the reaction chain as a series of processes whereby the oxidation of one sulfite ion induces the oxidation of another, and so on. The assumption would be, then, that in the presence of the alcohol this sometimes leads, instead, to

---

[1] Charlotte Elizabeth Procter Fellow at Princeton. This work was also in part carried out with the aid of an American-Scandinavian Fellowship at the Nobel Institute, Stockholm.

[2] Research Associate in Chemistry, Princeton University.

[3] Backstrom, THIS JOURNAL, 49, 1460 (1927).

[4] (a) Bigelow, *Z. physik. Chem.*, 26, 493 (1898); (b) Titoff, *ibid.*, 45, 641 (1903), and others.

[5] Bäckström, *Medd. Kgl. Vetenskapsakad. Nobelinst.*, 6, No. 16 (1927).

[6] Compare the theories of Dhar, *Proc. Acad. Amsterdam*, 23, 1074 (1921); *Z. anorg. Chem.*, 122,146 (1922), and Moureu and Dufraisse, *Compt. rend.*, 176,624 (1923), linking inhibitory power and oxidizability.

an induced oxidation of an alcohol molecule, and that this reaction is incapable of inducing further oxidations.?

In view of these considerations, it was decided to make a study of the oxidation of sulfite solutions in the presence of alcohols, in order to see whether the oxidation of the sulfite is accompanied by an induced oxidation of the alcohol, and, if so, whether the extent of this reaction is in accordance with the theory.

Theoretical

Bäckström found that his results on the rate of oxidation of sulfite solutions in the presence of alcohols could be expressed by the formulas

$$v_d = \frac{k_1}{kC + k_2} \tag{1}$$

$$v_l = k_3 v_d = \frac{k_3 k_1}{kC + k_2} \tag{2}$$

where v_l = light rate; v_d = dark rate; C = concn. of alcohol and k_1, k_2, k_3 and k are constants. The value of k depends on the nature of the alcohol and is a measure of its relative inhibitory power. The formulas express the facts that under a given set of experimental conditions the ratio between the rates of light and dark reaction remains constant, independent of the nature and concentration of the alcohol present, and that both rates are inversely proportional to a sum of two quantities, one being a constant, k_2, and the other proportional to the concentration of the inhibitor. The form of the equations and the complete analogy between light and dark reactions which they reveal indicate that the presence of the alcohols does not affect the number of chains *started* per unit time, but that they act solely by breaking the reaction chains.[8]

The fact that the chain length is inversely proportional to the factor $(kC + k_2)$ shows that the chains may be broken in two ways: (1) by the alcohol, its activity in breaking the chains being proportional to its concentration, C, and its relative inhibitory power, k, or (2) due to some other cause represented by the constant k_2. In the present paper we are concerned only with the former of these two processes.

In view of what was said in the preceding section, we shall now make the assumptions (1) that the alcohol is oxidized in breaking the reaction chains, and (2) that this induced oxidation is completely incapable of carrying on (that is, always breaks) the reaction chains. Let us then consider what results we should expect under different experimental con-

---

[7] Or, at least, less efficient than the corresponding reaction involving a sulfite ion.

[8] This is in agreement with the fact that they were present only in small concentrations and that, with one exception, they do not absorb the activating light. Consequently, in neither thermal nor photochemical reaction would they be expected to affect the **primary** process by which the reaction chains are started.

ditions. For convenience we shall assume that we are dealing with *iso*-propyl alcohol.

Every time a chain is broken by the alcohol, an acetone molecule will be formed. If we call the total number of chains started and broken per minute n, then the number of chains broken in that time by the alcohol will be $n[kC/(kC + k_2)]$, and this number of acetone molecules will be formed per minute. Since the velocity of sulfite oxidation V is expressed by the formula $V = k_1/(kC + k_2)$, it follows that the amount of acetone formed in a given time will always be proportional to CV, the product of velocity and inhibitor concentration.

At small inhibitor concentrations this product increases with increasing values of C, and the rate of acetone formation will increase in proportion.

At large inhibitor concentrations, on the other hand, where k_2 is negligibly small compared to kC, this product becomes virtually constant, independent of the alcohol concentration. In this region practically all the chains are broken by the alcohol. Increasing the alcohol concentration causes the chains to be broken sooner and, therefore, lowers the rate of sulfite oxidation, but the *number* of chains broken remains the same, and the amount of alcohol oxidized in a given time will therefore remain constant, independent of its concentration.

For the same reasons the number of alcohol molecules oxidized in a given time will be the same for different alcohols. The only difference will be that the amounts of these alcohols which have to be added in order to reach the region where k_2 can be neglected will vary inversely as their specific inhibitory powers, k.

This reasoning applies equally well to mixtures of alcohols in a given solution. They will be oxidized in proportion to their concentrations and relative inhibitory powers, but the total number of molecules oxidized in a given time will still be the same. All of this will, of course, be true only if the formula continues to be valid at high inhibitor concentrations; that it does is shown by our results.

The predictions above apply equally to the thermal and the photochemical reactions. In the case of the latter still another prediction may be made, namely, as to the number of alcohol molecules oxidized; in the region of constant *CV* it should be equal to the number of light quanta absorbed by the solution. This is assuming, however, that every absorbed light quantum starts a reaction chain, an assumption which is not necessarily correct, but which can be tested by experiments of this kind. If it is correct, that is, if the quantum efficiency actually evaluates the chain length of the photochemical reaction, then we should also expect it to measure the chain length of the thermal reaction. On this basis we may predict approximately the quantity of alcohol which should be oxidized, in the region of constant *CV*, by dividing the rate of oxidation of the pure sulfite solution by the value found by Backstrom for the quantum efficiency in the absence of inhibitors, namely, about 50,000 molecules of oxygen reacting per $h\nu$. The thermal oxidation rate of a pure sulfite solution under the conditions of our experiments was about 5 cc. of oxygen absorbed per minute per 10 cc. of solution, which leads to a value of about 0.000025 mole of alcohol oxidized per liter per hour.

These and other consequences of the theory were subjected to experimental test and were found to be completely verified except that the results indicate that two alcohol molecules, rather than one, are oxidized in the process of breaking a chain. This would, of course, not materially change the argument presented above. The inhibitors used were *iso*propyl, *sec.*-butyl and benzyl alcohols.

Materials

Water.—Tap water was distilled a few minutes before use into Pyrex flasks from a tin-lied still and block-tin condenser. Precautions were taken to use this water throughout all operations.

Sodium Sulfite.—Merck's C. P. crystals of $Na_2SO_3 \cdot 7H_2O$ were recrystallized from pure water four times. The third and fifth crystallizations gave identical oxidation rates, so there was no advantage in crystallizing any further.

Isopropyl Alcohol.—Standard Oil Company product. All the ordinary methods for removing acetone from isopropyl alcohol failed for this research. For example. with the usual bisulfite method,[9] it was extremely difficult to lower the acetone content of isopropyl alcohol below 0.001%, whereas it was necessary in this work to use alcohol containing less than 0.0001% of acetone. The following method therefore was developed and found to be a simple and direct method for removing very minute traces of ketones from the lower boiling alcohols. Several liters of the alcohol was refluxed with 2 g. of *p*-nitrophenylhydrazine per liter for several hours on a water-bath. Nitrogen bubbled through the solution during refluxing served both to stir the solution and to exclude oxygen. At the end of this time the alcohol was distilled over in a stream of nitrogen, using a 2-foot fractionating head. It contained less than 0.0001% of acetone; b. p. 81.9–82.9'.

Secondary Butyl Alcohol.—Standard Oil Company product. It received the same treatment as the isopropyl alcohol; b. p. 99.7–99.8°.

Benzyl Alcohol.—Merck's C. P. alcohol was used without further purification. It contained less than 0.0001 M benzaldehyde per liter as shown by Schiff's test.

Acetone.—Redistilled Merck's C. P. grade.

Methylethyl Ketone.—Eastman Kodak Company product. It was redistilled twice: shaken three times with equal volumes of a saturated solution of pure sodium chloride, in which it is insoluble, to remove acetone.[10] Subsequent distillation of the ketone layer yielded a pure methylethyl ketone, free from acetone.

Benzaldehyde.—Kahlbaum's DAB5 benzaldehyde was redistilled in an atmosphere of nitrogen. It contained less than 0.01% of benzoic acid, as determined by titration with sodium hydroxide in the presence of phenolphthalein.

Ethyl Alcohol.—It gave a coloration with Schiff's reagent corresponding to less than 0.001% of benzaldehyde.

---

[9] Marshall, J. *Chem. Soc.*, *89*, 1375 (1906).

[10] Price, J. *Soc. Chcm. Ind.*, 115, 1118 (1919).

Experimental

The apparatus consisted of a shaker which turned a set of glass-stoppered, narrow-mouthed 125-cc. bottles end-over-end at about 180 revolutions per minute. Each of these was charged with 20 cc. of 0.6 M sodium sulfite solution, buffered by the addition of 0.01 equivalent per liter of sulfuric acid, and containing varying quantities of alcohol. These solutions had the same composition as in Backstrom's work. The bottles were then filled with oxygen and the glass stoppers sealed in with paraffin. Preliminary experiments showed that during the above operations, consuming about fifteen minutes for a set of six bottles, the oxidation was negligible.

The strength of the sulfite was determined by titration with $N/2$ sulfuric acid, using brom-cresol green as indicator, as in Backstrom's work. Extreme precautions were taken in order to obtain reproducible results by preparing the distilled water and all solutions immediately before use and by washing all glassware repeatedly with distilled water to remove all traces of impurities.

The length of the shaking period, generally from two to thirty-five hours, was regulated to be such that less than 1.5 millimoles per 10 cc. of sulfite was oxidized. At the end of this period, 5 cc. of the sulfite was titrated with $N/2$ sulfuric acid, as above, and the quantity of sulfite oxidized obtained from this value. Other samples were immediately removed from the bottles and tested colorimetrically for the aldehyde or ketone formed, using the methods given below.

Throughout the run the average temperature of the room was 21 ± 0.5°, orientation experiments on the temperature coefficients of the sulfite and alcohol oxidations showing that the maximum error from temperature fluctuation was about 2%.

Dependence of Oxidation Rate on Experimental Conditions.—Preliminary measurements were made in a specially constructed shaking apparatus which permitted a study of the dependence of the oxidation rate on shaking conditions, volume of solution, and oxygen pressure. It was found that as the "reactivity" of the solution is decreased, by removing positive catalysts or adding increasing quantities of inhibitor, the oxidation rate (in moles per unit volume per unit time) becomes virtually independent of all these factors, including oxygen pressure.[11] The oxidation rate of a strongly inhibited solution, as directly observed in cc. of oxygen absorbed per minute at the working pressure, is thus four times higher at $^1/_4$ atm. than it is at 1 atm.

As a result of these experiments it may be stated that (with very few exceptions) the values given in this paper represent true oxidation rates, in the sense that neither an increase in oxygen pressure nor an increased shaking efficiency would have raised the results.

These preliminary experiments also included a study of the oxidation rate as a function of the concentration of the solution. It was found that the oxidation of a pure sulfite solution proceeds more slowly the more concentrated the solution, a fact which has previously been observed by Milbauer and Pazourek.[12] In accordance with this the rate increases

---

[11] This confirms an observation by Reinders and Vles, *Rec. trav. chim.*, *44*, **249** **(1925).**

[12] Milbauer and Pazourek, Bull. *soc. chim.*, *31*, **676** **(1922).**

steadily during a single run, as the sulfite concentration decreases, until a sudden drop occurs when the reaction is almost complete.

These facts are of great theoretical interest and will be investigated further in a more systematic study of sulfite oxidation.

Colorimetric Determinations

Since the quantity of alcohol oxidized in a run is of the order of 0.0005 millimole/10 cc./hour, the problem of measuring this change is of course the difficult feature of this research. The literature supplies tests only one-tenth as sensitive as are needed here. The following colorimetric methods were therefore developed, and if carried out as described will give accuracies of determinations as listed in Table II.

Acetone

Colorimetric Determinations in Concentrations of 0.00005 M to 0.002 M.—A development of the Kolthoff modification[13] of the Fabinyi-Frommer method[14] was found applicable. The test is specific for acetone, no color being given by methylethyl ketone or aromatic ketones.

Reagents.—The following solutions are employed: 10% vanillin in methyl alcohol, Merck's C. P. (not ethyl alcohol at these dilute acetone concentrations); should be made up fresh every few days; a potassium hydroxide solution, 100 g. of potassium hydroxide in 60 cc. of water; a series of standard acetone solutions made by dissolving 1 cc. of freshly distilled acetone in water and diluting to approximate concentrations of 0.004 M, 0.002 M, 0.0018 *M*, 0.0012 M, 0.0006 *M*, 0.0003 M and 0.00015 *M*, each solution containing 0.02 equivalent of sulfuric acid per liter.[15] The standards are then accurately determined by titration with *N*/100 thiosulfite and iodine, by the well-known Messinger method.[16] The strength of the standard acetone solutions fell less than 1% during two weeks, as shown by titrations.

Preparation of Standard and Unknown Test Solutions.—In a test the standard solution consists of 1 cc. of standard acetone solution, 1 cc. of 1.2 M sodium sulfite solution arid the same quantity of alcohol as in the unknown. The latter is made up by diluting 2 cc. of solution to be tested to a volume equal to that of the standard solution. The media of unknown and standard will then be exactly alike, differing only in acetone content. The color test is not affected by the extent to which the sodium sulfite in the unknown has been oxidized.

The Test.—Three unknown samples falling between the limits of two standard solutions may be tested conveniently at a time. Run 2 cc. of potassium hydroxide from a 10-cc. graduated pipet into each of the five tubes to be tested and swirl momentarily. Then into each run 1 cc. of the vanillin solution from a 5-cc. graduated pipet, shake thoroughly and place the five test-tubes simultaneously in a water-bath at the

---

[13] Kolthoff, *Pharm. Weekblad,* 55, 1021 (1918); Csonka, *J. Biol. Chem.,* *27,* 209 (1916).

[14] Fabinyi, *Chem. Centr.,* 1900, ii, 302; Frommer, *Ber. Klin. Woch.,* 42, 1008 (1905); Bohrisch, *Pharm. Centr.,* 48, 207 (1907).

[15] According to Folin and Denis, *J. Biol. Chem.,* 18, 263 (1914), the sulfuric acid also helps to prevent polymerization of the acetone in the standards.

[16] J. Messinger, *Ber.,* 21, 3366 (1888); *J. Biol. Chem., 43,* 43 (1920), and *J. Soc. Chem. Ind.,* 10, 166 (1891).

proper temperature. Allow to stand for exactly twenty minutes. In the meantime prepare five test-tubes each containing 10 cc. of water. Upon removing the acetone tubes from the water-bath immediately mix the water in the test tubes with the contents of the acetone tubes. The sulfates and sulfites which were precipitated by the concentrated potassium hydroxide will then redissolve, permitting a comparison of the reddish brown colors in a colorimeter. The above experimental procedure minimizes the time consumed between addition of reagents to the test solution and colorimeter readings, so that the colors in all five tubes will be strictly comparable. The readings are completed within fifteen minutes after removing the tubes from the bath.

The temperature of the water-bath is most important in obtaining reproducible results. A bath with thermoregulator attachment was used, giving the desired temperatures to within ±0.1°. For acetone concentrations within the range 0.00005 M to 0.0005 M, 65° was found to be the temperature at which the bath should be kept. For higher concentrations of acetone, between 0.0005 and 0.002 *M*, 50° should be used.

The colorimeter was of the standard DuBoscq type, Bausch and Lomb 1924 model. The colorimeter settings are plotted and the value of the unknown is determined graphically. Thus when the standards 0.0001 and 0.0002 *M* acetone give colorimeter readings of 50 and 30, respectively, a colorimeter setting of 40 would correspond to 0.00015 M acetone. While this method is not absolutely exact when the color does not vary directly with the acetone concentrations, the values it yields, nevertheless, fall well within the limits of error given in Tables I and II, where a typical set of colorimeter readings is presented.

TABLE I

TYPICAL COLORIMETER READING DATA

Acetone concn., *M*/l.	Colorimeter readings, a	Aa	b	Av. error in acetone detns. throughout the range, % (*c*)
0.002	26	24	−0.50	11.3
.001	50			
.00030	31	19	±0.75	±2.6
.00015	50			
.000150	38	12	±1.00	±5.5
.000075	50			

Aa = difference between colorimeter readings; that is, the number of colorimeter units representing a change from $^2/_3$ to $^4/_3$ the average acetone concentration in each range.

b = error of reproducibility of lower colorimeter settings, expressed in colorimeter units. (Higher setting always at 50.0.)

c = $(2/3)(b/\Delta a) \times 100$.

TABLE II

TYPICAL COLORIMETER READING DATA

Molarity of aldehyde or ketone	Average exptl. error, *c* %		
	Acetone	Methylethyl ketone	Benzaldehyde
0.005 to 0.002	...	...	±1.1
.002 to .001	±1.3	...	±1.7
.001 to .0005	...	±1.4	±3.8
.0005 to .0002	±2.6	...	±7.0
.0002 to .0001	...	±4.6	...
.0001 to .00005	±5.5	−6.0	...

Tests conducted in the presence of 0.6 *M* Na_2SO_3.

Methylethyl Ketone

The same procedure was employed as for the acetone, with the following changes: the vanillin in methyl alcohol was replaced by a 10% solution of salicylaldehyde in ethyl alcohol. The temperature of the bath was kept at 40 ±1°, since at above 60° the accuracy of the determination fell off rapidly at these low concentrations. Upon removal from the bath, instead of diluting with 10 cc. of water as was done in the acetone test, 15 cc. of a 20% by volume ethyl alcohol solution in water was added, This concentration was sufficient to dissolve the sulfite and salicylaldehyde; other proportions of alcohol and water will precipitate one or the other of the ingredients.

The comparison of the greenish-yellow tints obtained with the standards is done exactly as in the case of acetone, standard solutions being 0.002, 0.001, 0.0005 and 0.0002 *M*/liter, respectively, each containing 0.02 equiv. of sulfuric acid per liter. They, too, were accurately standardized by titrating with *N*/100 thiosulfate and iodine by the Messinger method.[16]

See Table II for the accuracy of the determinations.

Benzaldehyde

The sensitivity of Schiff's reagent[17] has long been known, and was employed by Woodman and Lyford[18] in determining benzaldehyde in minute quantities. However the much smaller concentrations of benzaldehyde obtained in this work required a refinement of their method.

Reagents

Schiff's Reagent.—The less sulfur dioxide present in the Schiff's reagent, the more sensitive is the test, although some sulfur dioxide is necessary for the color reaction.[19] The following procedure was found to work satisfactorily down to 0.0002 M benzaldehyde solutions. Bubble sulfur dioxide into 100 cc. of water for about five minutes and determine the amount absorbed by measuring the increased weight of the solution. Add a volume of this solution corresponding to 0.60 g. of sulfur dioxide to 0.17 g. of rosaniline hydrochloride in 50 cc. of water in a 250-cc. glass-stoppered volumetric flask. Allow to stand for one hour, shaking at frequent intervals, by which time most of the color will have disappeared. Fill up to the mark and use immediately. Fresh solutions should be made up every six hours when testing benzaldehyde in the ranges 0.0001 to 0.0005 mole/liter, but the reagent is good for several days when testing higher concentrations.

Aldehyde-Free Ethyl Alcohol.[18,20]—By distilling alcohol from solid potassium hydroxide (80 g./liter) an alcohol was obtained which gave a negligible coloration with Schiff's reagent under the conditions employed below.

Standard benzaldehyde solutions were made by successively diluting 10.00 cc. of benzaldehyde with aldehyde-free alcohol to give 0.005 0.002, 0.001, 0.0005 and 0.0002 *M* benzaldehyde solutions. These solutions will keep several months when stored in amber bottles.

Separation from Sulfite.—Before applying the Schiff's test, the aldehyde was separated from the sulfite by distillation. It was found that if 10 cc. of the solution containing partially oxidized sulfite and traces of benzaldehyde was distilled, the first

---

[17] Schiff, *Compt. rend.*, 61, 45 (1865).

[18] Woodman and Lyford, THIS JOURNAL, 30, 1607 (1908).

[19] Wieland and Schiering, *Ber.*, 54, 2527 (1921).

[20] See purification processes for ethyl alcohol in Tolman, THIS JOURNAL, 28, 1625 (1906).

5 cc. of distillate contained all of the benzaldehyde. When the PH of the solution was changed slightly from its original value[3] of PH = 8.4, the benzaldehyde still came over quantitatively, but at PH = 4.3, where all of the sulfite is present as the bisulfite, or at very high *PH's* (13) only about 70% of the benzaldehyde was recovered, possibly due to the stability of the bisulfite–benzaldehyde compound in the one case or the Cannizzaro reaction in the other.

A number of test-tubes 18 × 150 mm. were constricted in the middle to about 7.0 mm. inside diameter and graduated to hold exactly 10 cc. up to a mark on the constriction. Into one of them 5 cc. of aldehyde-free alcohol was run, and a 10-cc. sample solution distilled over in an atmosphere of nitrogen into the alcohol until the mark on the constriction was reached; 5 cc. of distillate was thereby collected. The volume caught could be reproduced to within 1% by this method. The benzyl alcohol present in the sample also distilled over, but it neither oxidized nor introduced any error in the benzaldehyde determination, as shown by blank tests. The mixture was then shaken, and the tube placed in an ice-bath at 0° for one minute along with two tubes containing standard solutions. These latter were made by adding 5 cc. of standard benzaldehyde solutions to 5 cc. of water; 2.5 cc. of the special Schiff's reagent, similarly cooled, was added to each of the three tubes, and the contents thoroughly shaken and allowed to stand at 0° for thirty minutes. At the end of this time their reddish pink colors were compared in the colorimeter. The strengths of the unknowns were determined graphically as with acetone; the accuracy is given in Table II.

Results

At High Inhibitor Concentrations.—The results, summarized in Table III, verify the predictions made in the introduction. The detailed experimental data are given in Tables IV, V and VI.

TABLE III

SUMMARY OF RESULTS

Alcohol	*C*, concn. range of alc., where CV = *K* ±15% mole/l.	Incr. in alc. concn.	*CV* throughout range × 10^4 ±15%	Inhib. power k of alc. (from *CV*)	Oxid. prod., mole formed per liter per hour ±15%	
Isopropyl	0.05 to 1.5	30-fold	34	3.0	Acetone	0.000046
Sec.-butyl	0.150 to 1.8	12-fold	103	1	Methyl-ethyl-ketone	0.000049
Benzyl	0.0073 to 0.167	23-fold	2.8	37	Benzaldehyde	0.000048

TABLE IV

THE INDUCED OXIDATION OF *ISO*PROPYL ALCOHOL

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Acetone formed × 10^4	V × 10^4	CV × 10^4	Acetone × 10^4
0.025	2.5	0.269	0.87	1080	27	0.35
.025	2.5	.237	.85	950	24	.34
.050	2.5	.154	1.04	616	31	.42
.050	2.5	.143	0.92	572	29	.37
.050	2.0	.115	.85	575	29	.42
.100	5.0	.165	2.4	330	33	.48
.100	5.0	.167	2.3	334	33	.47
.100	5.0	.180	2.5	360	36	.50

TABLE IV (Concluded)

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Acetone formed $\times 10^4$	V $\times 10^4$	*CV* $\times 10^4$	Acetone $\times 10^4$
.150	5.0	.131	2.4	262	39	.48
.150	5.0	.123	2.5	246	37	.50
.250	5.0	.072	2.4	144	36	.48
.250	5.0	.068	2.3	136	34	.46
.250	5.0	.083	2.2	166	41	.45
.250	10.0	.130	4.4	130	32	.44
.250	10.0	.139	4.4	139	35	.44
.250	10.0	.130	4.2	130	32	.42
.375	10.0	.089	4.3	89	33	.43
.375	10.0	.112	4.3	112	42	.43
.500	10.0	.056	4.2	56	28	.42
.500	10.0	.060	4.0	60	30	.40
.500	10.0	.075	4.5	75	37	.45
.500	21.0	.129	9.6	61	31	.45
.500	21.0	.127	10.2	60	30	.48
1.00	21.0	.069	11.2	33	33	.53
1.00	21.0	.069	11.7	33	33	.56
1.50	21.3	.056	10.6	26	39	.49
1.50	21.3	.059	11.2	28	42	.52
2.50	27.0	.050	18.3	19	46	.67
2.50	27.0	.048	17.8	18	44	.66
				Averages	34	.46

V = decrease in sulfite concentration per hour. In computing averages, the 2.5 M and 0.025 M values were omitted. All concentrations expressed as moles per liter.

TABLE V

THE INDUCED OXIDATION OF SECONDARY BUTYL ALCOHOL

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Ketone formed $\times 10^4$	V $\times 10^4$	CV $\times 10^4$	Methylethyl ketone $\times 10^4$
0.15	2.05	0.175	0.92	850	128	0.45
.25	4.0	.186	2.1	465	116	.53
.25	4.0	.196	2.1	490	122	.52
.30	4.0	.141	~~2.0~~	~~353~~	~~106~~	~~.49~~
.30	4.0	.121	1 6	303	91	.40
.45	4.0	.101	2.0	253	114	.50
.45	4.0	.106	1.8	266	119	.46
.45	6.0	.131	2.2	218	98	.37
.45	6.0	.141	2.5	235	106	.41
.60	6.0	,106	2.6	177	106	.43
.60	6.0	.106	2.7	177	106	.45
1.00	14.0	.123	7.8	88	88	.56
1.00	14.0	.128	7.3	91	91	.52
1.20	14.0	.111	7.8	79	95	.55
1.20	14.0	.118	8.3	84	101	.59

TABLE V (*Concluded*)

Alc. C	Hours shaken	Observed values Sulfite ox.	Ketone formed $\times 10^4$	Values calcd. to one hour V $\times 10^4$	*CV* $\times 10^4$	Methylethyl ketone $\times 10^4$
1.50	15.5	.088	7.8	57	85	.50
1.50	15.5	.103	8.5	66	100	.55
1.80	15.5	.088	8.4	57	102	.54
1.80	15.5	.080	8.1	52	93	.52
				Averages	103	.49

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

TABLE VI

THE INDUCED OXIDATION OF BENZYL ALCOHOL

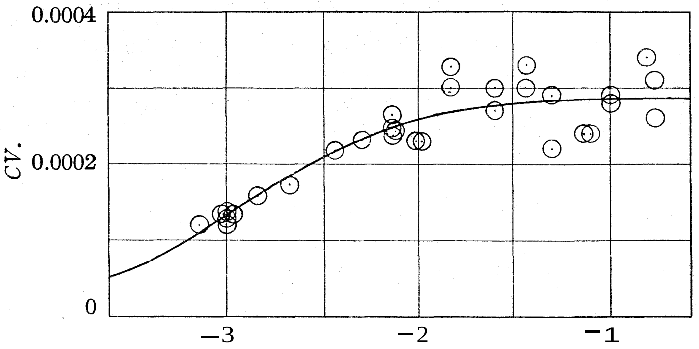
Alc., C	Hours shaken	Observed values Sulfite ox.	Benzaldehyde formed $\times 10^4$	Values calcd. to one hour V $\times 10^4$	CV $\times 10^4$	Benzaldehyde $\times 10^4$
0.00735	2.62	0.086	1.1	330	2.4	0.42
.00735	2.92	.096	1.1	330	2.4	.38
.0147	3.73	.076	1.6	200	3.0	.43
.0147	4.30	.096	2.0	220	3.3	.46
.025	10.25	.122	4.9	119	3.0	.48
.025	11.25	.120	6.3	107	2.7	.56
.037	12.90	.106	6.8	82	3.0	.53
.037	13.20	.116	8.4	88	3.3	.64
.050	18.10	.080	7.7	44	2.2	.43
.050	19.00	.110	10.4	58	2.9	.55
.075	22.15	.070	9.8	32	2.4	.44
.075	24.66	.080	13.0	32	2.4	.53
.10	31.00	.087	17.9	28	2.8	.58
.10	36.38	.107	15.1	29	2.9	.42
.15	37.50	.086	19.0	23	3.4	.51
.167	38.00	.071	18.0	19	3.1	.47
.167	61.00	.095	24.0	16	2.6	.39
				Averages	2.8	.48

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

In order to prove that the oxidation of the alcohol was definitely induced by the oxidation of the sulfite, 5-cc. samples of alcohol solutions were shaken with 15 cc. of (1) water, (2) N/2 KOH and (3) phosphate buffer of PH = 8.4, the initial PH of the sulfite solutions in Table IV. The alcohol solutions added were: benzyl, 0.04 M; *sec.*-butyl, 1.0 M; isopropyl, 1.0 M. In addition to these, 15-cc. samples of a previously oxidized 0.8 M sulfite solution were shaken with 5 cc. of 0.04 M benzyl, of 0.5 M *sec.*-butyl and of 0.25 M isopropyl alcohol. With a shaking time of seventy-two hours, less than the following quantities of alcohol were oxidized: benzyl alcohol, 0.0002 mole/liter; *sec.*-butyl alcohol, 0.00005 mole/liter;

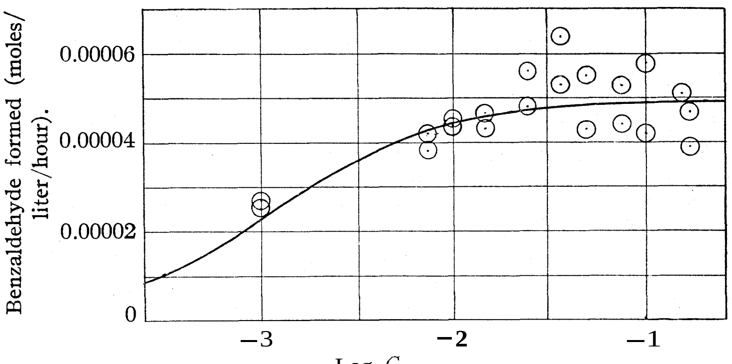
isopropyl alcohol, 0.00005 mole/liter, compared with the amount normally oxidized in seventy-two hours: (Table III) 0.00356 mole/liter.

At Low Inhibitor Concentrations.—In these experiments, which were made with benzyl alcohol, the shaking period was necessarily so short as to produce only a very minute quantity of benzaldehyde in the sulfite sample. By successive distillations of a 90-cc. sample (six 15-cc. samples from a set of bottles in a normal run), however, the benzaldehyde was obtained in concentrations sufficiently large to permit of accurate colorimetric analysis.



○, values observed; ——, values calculated from $V = 0.00029/(C + 0.0012)$.

Fig. 1A.



○, values observed; ——, values calculated from: Benzaldehyde formed = CV × 0.48/2.8 (see Table VI).

Fig. 1B.

The results given in Table VII, and represented in the upper graph of Fig. 1, show that the rate of sulfite oxidation obeys a formula of the type discussed in the introduction, namely, $V = 0.00029/(C + 0.0012)$, throughout the entire range studied.

Table VIII establishes that the dropping off in CV at lower alcohol concentrations is accompanied by a corresponding decrease in benzaldehyde formed. This is demonstrated in Fig. 1, where the lower graph summarizes the results on the amount of benzaldehyde formed and shows that it is given within experimental error by the expression (0.48/2.8) X CV throughout the range of benzyl alcohol concentrations studied.

TABLE VII

INHIBITION BY BENZYL ALCOHOL OF SULFITE OXIDATION

Alcohol, C	Hours	Observed values Sulfite oxidized	Values calcd. to one hour $V \times 10^4$	$CV \times 10^4$
0.00072	0.33	0.055	1650	1.20
.00100	1.00	.130	1300	1.30
.00100	1.00	.120	1200	1.20
.00100	1.00	.135	1350	1.35
.00144	1.00	.110	1100	1.58
.0021	1.37	.113	825	1.73
.0036	2.00	.121	610	2.20
.0050	2.6	.120	460	2.30
.0072	2.85	.098	340	2.50
.0072	2.85	.105	370	2.65
.00735	2.62	.086	330	2.40
.00735	2.92	.096	330	2.40
.0147	3.73	.076	200	3.00
.0147	4.30	.096	220	3.30
		vs.		
.0147	3.73	.076	220	
to	**to**	**to**	**to**	**2.8**
.167	61.00	.120	16	

(Averages, see Table VI)

V = **decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.**

TABLE VIII

CV AND ALDEHYDE FORMED AT LOW CONCENTRATION

Benzyl alcohol concn. C	$CV \times 10^4$	Benzaldehyde formed $\times 10^4$	Ratio of $\frac{0.001\ M\text{ rate}}{0.01\ M\text{ rate}}$ for CV	for aldehyde
0.01	2.30	0.44		
.01	2.30	.45		
			$\frac{1.36}{2.30} = 0.59$	$\frac{0.26}{0.445} = 0.58$
.001	1.37	.25		
.001	1.35	.27		

Mixtures of Inhibitors

Benzyl Alcohol–Isopropyl Alcohol.—Experiments were made with sulfite solutions containing equal molal quantities of benzyl and *iso*propyl alcohols. Five cc. of the solutions shaken was titrated to determine sulfite oxidized, 2 cc. was removed and tested for acetone and, finally, a 10-cc. sample was tested for benzaldehyde. Preliminary measurements showed that the presence of as much as 0.01 *M* benzaldehyde or 0.02 M acetone had no effect on the accuracy of a colorimetric determination of acetone or of benzaldehyde, respectively, carried out as described above.

Tables IX and X show that the inhibitory power of a mixture is an additive property and confirm the prediction in the introduction as to the relative amounts oxidized of the two alcohols.

TABLE IX

*Iso*PROPYL ALCOHOL–BENZYL ALCOHOL MIXTURES

			Observed values		
Hours	Sulfite oxidized	Concn. of each alcohol	Benzaldehyde $\times 10^4$	Acetone $\times 10^4$	Ratio of benzaldehyde/acetone
16.05	0.165	0.025	7.6	0.56	14
16.05	.133	.025	6.7	.56	12
24.00	.146	.050	8.9	.72	12
40.20	.103	.100	17.0	1.17	15
40.20	.088	.100	14.4	1.08	13
				Average	13

TABLE X

VALUES CALCULATED TO ONE HOUR

Concn. of each alcohol	ΣkC[a] $\times 10^4$	V $\times 10^4$	ΣkCV[a] $\times 10^4$	Benzaldehyde $\times 10^4$	Acetone $\times 10^4$
0.025	0.338	103	35	0.47	0.035
.025	.338	83	28	.42	.035
.050	.675	61	41	.37	.030
.100	1.35	26	35	.42	.029
.100	1.35	22	30	.36	.027
		Averages	34	.41	.031
		Total inhibitor oxidized		0.44	

[a] k, the inhibitory power for isopropyl alcohol is here taken as unity, giving a value of **12.5** (Table III) for benzyl alcohol. Compare with the value of **13,** obtained above, Table IX, from the relative amounts oxidized.

Benzyl Alcohol–Hydroquinone Mixtures.—In this case most of the chains are broken by the hydroquinone, as is shown by the fact that the CV value for hydroquinone is practically independent of the presence of benzyl alcohol (see Table XII). The quantity of benzaldehyde formed was less than one-twelfth of that which would have formed in the absence of hydroquinone. It is a duplication of the phenomena observed in the benzyl alcohol–*iso*propyl alcohol mixtures.

Attention should be directed toward the increasing *CV* values for hydroquinone with increasing concentration of the latter in Tables XI and XII. Bäckström[3] had previously observed that hydroquinone and some other substances behave differently from the alcohols, apparently inhibiting the light reaction much more strongly than the dark reaction. The fact that these substances are themselves capable of reacting with oxygen, especially in alkaline solution, suggests that in these cases the phenomena are complicated by a direct oxidation of the inhibitor. The rate of this reaction would naturally increase with the concentration[21] which would account for the increasing values of CV; and the increase in the observed "dark rate" caused by this direct oxidation of the inhibitor, which would probably not be accompanied by a corresponding increase in the light rate, would give the impression that the light reaction has been suppressed to an abnormal degree. Since, in the present case, the oxidation rate was determined by measuring the decrease in sulfite concentration, and not the oxygen consumption—as in Bäckström's experiments—the observed facts can only be accounted for on this basis if the oxidation of hydroquinone involves a reaction with sulfite. It might, for instance, lead to the for-

TABLE XI

HYDROQUINONE–BENZYL ALCOHOL MIXTURES

Hydroquinone concn., C	Benzyl alc. concn., C'	Hours	Sulfite oxidized	V $\times 10^4$	CV $\times 10^4$	Average CV
0.05	0.05	4.8	0.021	44	2.2	2.2
.025	.025	5.1	.016	31	0.8	
.025	.025	15.4	.031	20	.5	0.7
.025	.025	16.8	.061	36	.9	
.0125	.0125	5.3	.018	34	.4	
.0125	.0125	15.8	.041	26	.3	.3
.0125	.0125	31.0	.046	15	.2	
.05	0	11.0	.053	48	2.4	2.4
.025	0	10.7	.020	19	0.5	0.6
.025	0	18.6	.050	27	.7	
.0125	0	4.0	.013	32	.4	
.0125	0	22.4	.033	15	.2	.3
.0125	0	22.4	.037	17	.2	

TABLE XII

RESULTS OF EXPERIMENTS

Concn. of hydroquinone and of benz. alc.	CV, hydroquinone alone $\times 10^4$	CV, hydroquinone + benz. alc. $\times 10^4$	Benzaldehyde formed per hour $\times 10^4$	Ratio $\frac{\text{benzyl alcohol (Table 6)}}{\text{benz. alc. + hydroquinone}}$ for CV	Ratio $\frac{\text{benzyl alcohol (Table 6)}}{\text{benz. alc. + hydroquinone}}$ for aldehyde
0.05	2.4	2.2	<0.04	1.3	>12
.025	0.6	0.7	$<.03$	4	>16
.0125	.3	.3	.04	9	12

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

---

[21] The true inhibitory power would therefore be more nearly given by the experiments at the low concentrations of inhibitor in Table XII. They indicate that the inhibitory power of hydroquinone is more than ten times that of benzyl alcohol.

mation of the hydroquinone sulfonates observed by Pinnow[22] in oxidized developer solutions.

Photochemical Measurements.—The applicability of the theory to the photochemical reaction was tested in a series of experiments with *iso*propyl alcohol. The apparatus consisted of a quartz shaker similar to that used in Bäckström's work, except that the tube was shaken horizontally. Conditions of shaking were such that, as shown by preliminary experiments, the oxidation rate of the sulfite was independent of volume of solution shaken, number of strokes per minute, length of stroke and oxygen pressure. The light from a Hanovia Quartz lamp, burning at 69 ± 0.5 volts and 3.5 ± 0.05 amperes was filtered through a chlorine–bromine filter, so that only wave lengths 2300 to 2800 Å. were transmitted, as shown by visual observation of the filtered light through a monochromator in the exit slit of which was placed a piece of uranium glass. This light illuminated about a 5-cm. length of the quartz shaker. Under these conditions the photochemical reaction was about fourteen times greater than the thermal reaction so that, within limits of error, the reaction measured could be considered entirely photochemical.

The results, given in Table XIII, are completely analogous to the ones previously obtained for the thermal reaction. Over a considerable range of high inhibitor concentrations, *CV* and alcohol oxidized remain constant. The ratio between *CV* and acetone formed (510/6.6 = 77) is the same as was found for the thermal reaction, Table IV (34/0.46 = 74); that is, in a solution of a given composition the chain length is the same whether the chains are started thermally or photochemically.

TABLE XIII

THE INDUCED OXIDATION OR *ISO*PROPYL ALCOHOL: PHOTOCHEMICAL REACTION

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Acetone formed $\times 10^4$	V $\times$ 104	CV $\times 10^4$	Acetone $\times 10^4$
0.05	0.166	0.155	1.03	9300	470	6.2
.05	.166	.169	0.98	10200	510	5.9
.10	.166	.089	1.17	5400	540	7.0
.10	.25	.120	1.75	4800	480	7.0
.10	.33	.167	2.27	5100	510	6.9
.50	1.166	.117	8.2	1000	500	7.0
.50	1.00	.108	7.0	1080	540	7.0
1.50	3.25	.102	19.5	314	470	6.0
1.50	3.00	.116	19.8	387	580	6.6
2.50	4.00	.108	26.5	270	675	6.6
				Averages	510	6.6

V = decrease in sulfite concentration per hour. In computing averages the 2.5 M values were omitted. All concentrations expressed as moles per liter.

---

[22] Pinnow, *Z. Elektrochem.*, 19, 262 (1913).

Blank experiments in which there was no sulfite present in the solution showed that the direct photochemical oxidation of the alcohol was negligible (0.00001 in a blank against 0.00066 mole per liter per hour in a normal sulfite run).

Chain Length and Quantum Efficiency.—As was shown in Tables III to VI, the amount of alcohol oxidized, in the region of constant CV, is of the order of magnitude expected, being just about twice the predicted value of 0.000025 mole per liter per hour. This indicates the correctness of the assumption underlying the prediction, namely, that the chain length of the thermal reaction is equal to the photochemical quantum efficiency, but it does not constitute an accurate test since it is based on measurements on uninhibited sulfite solutions; these give high oxidation rates that are difficult to measure accurately and that vary considerably with shaking conditions. However, a more satisfactory comparison, utilizing the data for strongly inhibited solutions, gives the same result.[23] Bäckström's formula for the light rate,[3] when applied to a solution which is 0.1 *M* with respect to benzyl alcohol, gives a quantum yield of 64 molecules of oxygen or 128 of sulfite reacting per $h\nu$. On the other hand, the data in Table VI show that in a solution of this composition the number of sulfite molecules oxidized for every alcohol molecule oxidized is $28/0.48 = 58$, a figure which is of the same order of magnitude but which again indicates that in the process of breaking a reaction chain, two molecules of the alcohol are oxidized rather than one: this would make the chain length equal to $2 \times 58 = 116$. The question whether 1 or 2 molecules are oxidized in this process is of no importance to the arguments presented in this paper, but it is obviously of great importance to a complete elucidation of the reaction mechanism. By a repetition of the quantum efficiency measurements it is hoped to decide this question more definitely.

Utilizing the result of the preceding section, namely, that the chain lengths of thermal and photochemical reaction are identical,[24] we may state the above result in a different way by saying that, in the photochemical reaction $128/58 = 2.2$ molecules of benzaldehyde are formed for every quantum absorbed by the solution; that is, the induced oxidation of the benzyl alcohol obeys the Einstein photochemical equivalence law.

This is a result which is completely analogous to the one obtained by Cremer,[25] in a study of the photochemical hydrogen–chlorine combination in the presence of oxygen. Here oxygen acts as an inhibitor and

---

[23] This throws an interesting light on Bäckström's results on the quantum efficiency of the photosensitized reaction (ref. 5, pp. 26–29).

[24] No measurements were made on the induced oxidation of benzyl alcohol, in the photochemical reaction, since it was feared that the light absorption of the alcohol might introduce complications. Unlike the aliphatic alcohols, benzyl alcohol has an absorption spectrum extending farther toward the visible than that of the sulfite.

[25] Cremer, *Z. physik. Chem.*, 128, 285 (1927).

the reaction is accompanied by an induced, or "photosensitized," formation of water. This induced reaction was found by Cremer to be independent of the oxygen pressure and to obey the equivalence law, two molecules of water being formed for every light quantum absorbed by the chlorine.

Copper Accelerated Solutions.—It is well known that copper ions tremendously accelerate the oxidation of pure sulfite solution.[26] If the effect of copper ions is merely one of starting more than the usual number of sulfite chains per unit time, both CV and the quantity of benzaldehyde formed would be proportionately higher, but otherwise the phenomena observed for pure sulfite solutions would be unchanged.

Table XIV gives some results in the presence of 2.5 X 10^{-6} mole/liter of copper sulfate.[27] It shows that CV and the rate of benzaldehyde formation, are constant, independent of alcohol concentration, and that both have been proportionately increased over the normal values.

Table XIV

Copper Accelerated Reaction: the Induced Oxidation of Benzyl Alcohol

Alc. concn., C	Hours	Observed values		Values calcd. to one hour			Increase over the normal value (Table VI)	
		Sulfite ox.	Benzaldehyde $\times 10^4$	$V \times 10^4$	$CV \times 10^4$	Benzaldehyde	$CV/2.8 \times 10^{-4}$	Benzaldehyde/0.48×10^{-4}
0.025	1.0	0.028	1.4	280	7.0	1.4	2.5	2.9
.025	2.0	.060	3.3	300	7.5	1.65	2.7	3.4
.050	7.88	.118	13.0	150	7.5	1.65	2.7	3.4
.050	8.20	.118	9.0	144	7.2	1.1	2.6	2.3
.100	14.65	.108	17.5	74	7.4	1.2	2.6	2.5
.100	14.00	.099	16.5	71	7.1	1.2	2.5	2.5
					Averages		2.6	2.8

At higher copper concentrations, however, the results are more complex, due probably to the deficiency of the shaker in supplying oxygen at these high reaction rates, and possibly also to the limited solubility of the copper (as $Cu(OH)_2$?).[28]

It should be emphasized at this point that it is quite possible, as first suggested by Titoff,[4b] that a sulfite solution which is perfectly free from positive catalysts such as copper salts would not react with oxygen in the dark; but no satisfactory evidence has been presented to substantiate the idea of Luther and Titoff that the inhibitors act by combining with, or in some way destroying, this positive catalyst. Moreover, it seems

---

[26] Titoff, *Z. physik. Chem.*, 45, 641 (1903).

[27] Blank tests on solutions of 5 cc. of 0.04 M benzyl alcohol with 15 cc. of water; of potassium hydroxide; of phosphate buffer, $P_H = 8.4$; or of oxidized 0.8 N sulfite, all in the presence of 2.5×10^{-6} mole per liter copper sulfate, gave no benzaldehyde after fifty hours of shaking.

[28] Reinders and Vles, *Rec. trav. chim.*, 44, 249 (1925).

impossible to explain our results, as well as those of Backstrom, on this theory.[29]

Summary

It has previously been shown that the action of alcohols in inhibiting the oxidation of sulfite solutions must consist in the breaking of reaction chains, in the thermal as well as in the photochemical reaction. The present investigation leads to the conclusion that the mechanism of this process involves an induced oxidation of the alcohol, two molecules of the oxidation product (an aldehyde or ketone) being formed whenever a chain is broken.

The following experimental results, chiefly obtained for the thermal reaction, may be accounted for on this basis.

1. The oxidation of the sulfite induces an oxidation of the alcohols.
2. At low inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concentration.
3. At high inhibitor concentration the amount of alcohol oxidized per unit time is constant, independent of its concentration. This was shown to apply to the photochemical as well as to the thermal reaction.
4. In this concentration region the number of inhibitor molecules oxidized per unit time is quantitatively the same for different alcohols of widely different inhibitory powers.
5. Two alcohols present in the solution at the same time have an additive inhibitory effect. They are oxidized in proportion to their inhibitory powers, the total number of alcohol molecules oxidized being the same as when only one alcohol is present.
6. Copper sulfate accelerates the thermal reaction without altering the ratio of sulfite oxidized to alcohol oxidized.
7. The chain length is the same for the thermal and photochemical reaction and is equal to the photochemical quantum efficiency. This may also be expressed by saying that in the light reaction the induced oxidation obeys the Einstein equivalence law.

The alcohols used as inhibitors were isopropyl, *sec.*-butyl and benzyl alcohols. In order to determine quantitatively the minute traces of acetone, methylethyl ketone and benzaldehyde that were formed in the reaction, colorimetric tests were developed for concentrations to as low as 0.00005 mole per liter, about ten times as sensitive as those previously described in the literature.

Some experiments with hydroquinone gave results that suggest an ex-

---

[29] A recent investigation by Mason and Mathews, J. *Phys.* Chem., 30, 414 (1926), gave a result which is not consistent with our views on the role of copper in this reaction; they stated that copper sulfate acted as an inhibitor to the photochemical reaction. We have found, however, by a series of experiments with copper sulfate, that this does not hold true under our experimental conditions.

planation for the anomalous behavior of this substance as an inhibitor to the oxidation of sulfite solutions.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 191]

MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

BY WARREN P. BAXTER AND ROSCOE G. DICKINSON

RECEIVED JULY 30, 1928 PUBLISHED JANUARY 8, 1929

Introduction

The photochemical decomposition of nitrogen pentoxide into nitrogen dioxide and oxygen was first studied by Daniels and Johnston.[1] Their method of experimentation was to illuminate, with sunlight or light from a tungsten lamp, a glass bulb containing nitrogen pentoxide crystals immersed in ice water and measure the pressure increase attending the illumination. By the use of light filters these authors were able to demonstrate that only light of wave length shorter than 4600 Å. was effective in producing decomposition. They also established the important result that, at least with radiations in the neighborhood of the violet part of the spectrum, the presence of nitrogen dioxide is necessary for the reaction, that is, this decomposition of colorless nitrogen pentoxide is photosensitized by the brown dioxide.

Two important suggestions have been made as to the mechanism of this reaction. Fazel and Karrer[2] have advanced the hypothesis that a light quantum is absorbed by a nitrogen dioxide molecule, which is thereby raised to a higher quantum state, and that this excited molecule, NO_2', then makes a collision of the second kind with a pentoxide molecule, transferring energy of activation to the pentoxide molecule. The activated nitrogen pentoxide molecules subsequently decompose. Norrish,[3] on the other hand, has shown that nitrogen dioxide is decomposed by light from a mercury arc into nitric oxide and oxygen. He has accordingly suggested that in the sensitized decomposition of the pentoxide, the first reaction is the decomposition of the dioxide, and that this is then followed by a dark reaction between nitric oxide and nitrogen pentoxide, $NO + N_2O_5 = 3NO_2$. For this mechanism to play an important part in the pentoxide decomposition, it is necessary that the thermal reaction between nitric oxide and nitrogen pentoxide have a rate at least comparable with the rate of recombination of nitric oxide and oxygen. Busse

---

[1] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[2] Fazel and Karrer, *ibid.*, 48, 2837 (1926).

[3] Norrish, J. *Chem. Soc.*, 761 (1927).

and **Daniels**,[4] by mixing nitric oxide and nitrogen pentoxide and observing the immediate appearance of the brown dioxide, have shown that this reaction is indeed very rapid.

It is to be noticed that if photochemical equivalence obtained, the decomposition of two molecules of nitrogen pentoxide per quantum absorbed could result no matter whether the initially activated NO_2 molecule transferred its activation to an N_2O_5 molecule, or whether it reacted with another NO_2 molecule. For in the first case we might have $NO_2' + N_2O_5 = N_2O_5' + NO_2$, followed by $N_2O_5' + N_2O_5 = 4NO_2 + O_2$ or by $N_2O_5' = NO + NO_2 + O_2$ and $NO + N_2O_5 = 3NO_2$; while in the second case we might have $NO_2' + NO_2 = 2NO + O_2$ followed by $2(NO + N_2O_5 = 3NO_2)$. However, the authors have shown[6] that in the decomposition of the dioxide, various wave lengths are quite unequally effective; thus the yields expressed in molecules of oxygen produced per quantum absorbed were 0.0046, 0.36, and 0.77 for the wave lengths 4350, 4050 and 3660 Å., respectively. Since the decomposition of the dioxide depends so markedly on the wave length of the light used, measurement of the pentoxide decomposition with monochromatic light might distinguish between these two mechanisms. Should, for example, the radiation 4350 Å. prove to be effective in the pentoxide decomposition, this could hardly be explained by the Norrish mechanism because of the ineffectiveness of this radiation in decomposing the dioxide.

In the present paper are described measurements of the relative rates of nitrogen pentoxide decomposition produced by these three radiations and measurements of the relative rates of pentoxide and dioxide decomposition.

This investigation was aided financially from a grant made to Professor **A. A. Noyes** by the Carnegie Institution of Washington.

Experimental Arrangement

The present work was carried out at 0° with the reactants and products present only in the gas phase. The apparatus is shown in Fig. 1. The reaction vessel, A, made of Pyrex glass, was oblong shaped with flat sides 2.2 cm. wide and 6.5 cm. high. Three of these sides were silvered, while the front surface was unsilvered and served as a window for the entrance of light. The dicker-type glass-diaphragm gage, B, described by Smith and Taylor[6] was used to measure the pressure after the reaction chamber was sealed off at C and C'. Pressure readings were reproducible to 0.2 mm. or better. A Moll thermopile, mounted in a water-tight brass container with a glass window and a shutter, was rigidly fastened immediately beside the reaction vessel, as indicated at D. This was used to make relative measurements of light intensity during the illumination.

The thermostat, K, was a flat-sided glass jar. On the front of the thermostat was

---

[4] Busse and Daniels, THIS JOURNAL, 49, 1257 (1927).

[5] Dickinson and Baxter, *ibid.*, 50, 774 (1928).

[6] Smith and Taylor, *ibid.*, 46, 1393 (1924).

fastened a flat copper sulfate absorption cell 1.2 cm. in thickness in such a way as to have a pocket 2.2 cm. in thickness between the cell and the front of the thermostat. A light filter mounted on a brass sheet with an opening 4.5 cm. square was placed in this pocket; the space was then filled with water to minimize light reflection losses. These filters were for the isolation of the mercury radiations at 4350, 4050 and 3660 Å. and were the same as used previously.[7] A mercury arc lamp together with a reflector was placed immediately outside the copper sulfate cell and directly in front of the reaction vessel; the distance from the lamp to the reaction chamber was 6 cm. A shutter was provided between the lamp and the copper sulfate cell.

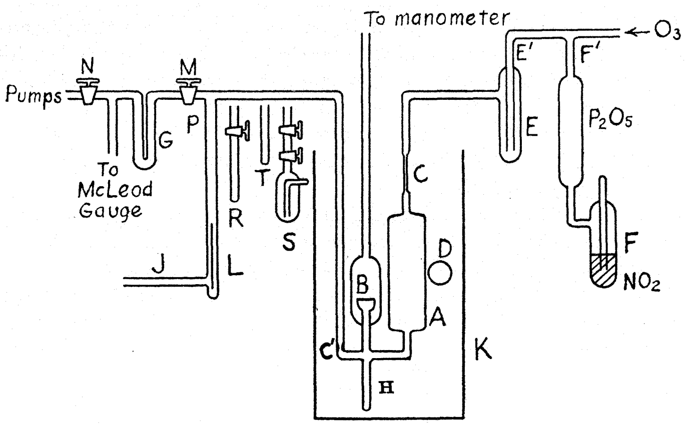


Fig. 1.

Temperature control was maintained by keeping the thermostat well packed with ice. A fine jet of air blown into a glass tube 1 cm. in diameter pumped water continuously from the bottom of the thermostat to near the top. A thermocouple with one junction near the bottom of the reaction chamber and the other in a Dewar tube filled with ice and water showed that the temperature was maintained constant to 0.1° or better.

The Experimental Procedure

Nitrogen pentoxide was prepared by oxidizing nitrogen dioxide in a stream of ozone and collecting the pentoxide in the trap, E, surrounded by ice and hydrochloric acid. The nitrogen dioxide had been previously prepared by heating c. p. lead nitrate in an all-glass apparatus, passing the gas evolved over phosphorus pentoxide and condensing it in the trap. F, using ice and salt. The ozone was prepared by passing tank oxygen over phosphorus pentoxide and then through a Siemen's ozonizer. During the pentoxide preparation the cock, M, was closed and the excess gases passed out through J.

When sufficient nitrogen pentoxide had been collected in E, the supply of nitrogen dioxide was sealed off at F' and the stream of ozone continued for a short time. The ozonizer was now turned off and, after sweeping out the ozone with oxygen, the apparatus was sealed at E'. A bulb of nitrogen dioxide was now placed in the tube, J, which was then sealed off. Liquid air was applied at E and G, the stopcock M opened and the whole system evacuated. The click gage was protected from breakage by evacuating both sides simultaneously. When the system was well evacuated, the bulb of nitrogen dioxide was broken by the magnetically operated plunger, L, the nitrogen dioxide im-

---

[7] Dickinson and Baxter, ref, 5, p. 778.

mediately freezing out in the trap, E'. After a final evacuation, the apparatus was sealed off at C'. Then ice-baths were placed around the reaction vessel and around E'. After the pressure had-risen sufficiently, the tube, C, was sealed off. In order to determine the original pressure of oxygen produced by decomposition on sealing off, liquid air was applied at the side-tube, H, and the pressure read. In no case was this pressure as large as 0.5 mm. The liquid air was now removed, the thermostat put in place, packed with ice and the initial pressure read.

The mercury arc was started and run for a time to become steady, pressure readings being taken at intervals. The shutter was now opened with pressure readings still being made during illumination. During this time measurements were made on the light intensity by reading the galvanometer connected with the thermopile when the shutter on the thermopile was opened and closed at intervals of one minute. The illumination was now discontinued but pressure readings were still made. The times of opening and closing the shutter were accurately noted. Another illumination was now carried out with a different filter interposed. In this way several illuminations could be made during a run with each of the wave lengths used before the supply of nitrogen pentoxide was exhausted.

The illuminations were continued until the nitrogen pentoxide was exhausted. The final total pressure was obtained from readings made several hours after the last illumination. The final pressure of oxygen was obtained by freezing out the nitrogen dioxide in the tube, H, with liquid air, measuring the pressure of uncondensed oxygen at room temperature; this measured pressure was first increased by 2% because of the fact that a definite volume of oxygen was at liquid-air temperature, and was then reduced to 0°.

Experimental Results

Fig. 2 shows the results of a typical series of successive illuminations (Nos. 3a, 3b and 3c) made with light of the wave lengths 3660, 4350 and 4050 Å., respectively. The ordinates are total pressure in mm. and the abscissas time in minutes; the periods during which illumination occurred are indicated on the plots. In these particular experiments the partial pressure of NO_2 was about 12 mm. and that of N_2O_5 about four times as great. The absorption, estimated from previous measurement, was probably greater than 60% in each case. The radiations 3660 and 4050 produced continuous pressure increases which ceased when the radiations were shut off. The radiation 4350 produced no detectable pressure increase although its intensity was more than three times that of the other radiations.

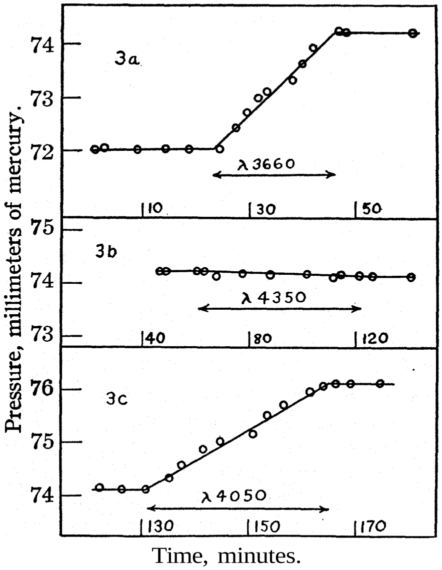


Fig. 2.

---

[8] Dickinson and Baxter, ref. 5, p. 780.

The results of these and other similar experiments are given in the first nine columns of Table I. In Cols. 3–6 are given the mean partial pressures of the gases present during each illumination; their calculation involved, in addition to the pressure measurements described above, the constant[9] for the equilibrium between NO_2 and N_2O_4 at 0°. The amount of nitrogen pentoxide decomposed is not proportional to the observed pressure increase, Δp_{total}, in different parts of a run. Instead, it may be shown that when the total pressure changes as a result of pentoxide decomposition

TABLE I

EXPERIMENTAL RESULTS WITH $N_2O_5 + NO_2$ AND WITH NO_2

No.	Wave length, Å.	p_{NO_2}, mm.	$p_{N_2O_5}$, mm.	$p_{N_2O_4}$, mm.	p_{O_2}, mm.	Intensity, cm. of scale defl.	Exposure, min.	Δp_{total} mm.	$-\Delta p_{N_2O_5}$ mm./10 min. per cm. defl.	$2\Delta p_{O_2}$ mm./10 min. per cm. defl.
4a	3660	4.1	42.0	1.5	0.7	6.44	20.8	2.8	0.24	0.25
4c		8.2	35.8	5.7	3.9	4.50	26.8	3.6	.39	.38
4d		11.2	29.4	10.7	7.2	4.54	43.7	5.5	.39	.42
3a		11.6	48.6	11.5	1.1	4.16	22.8	2.2	.33	.43
3d		14.4	41.0	17.7	5.0	3.60	33.2	3.2	.40	.45
2b		16.3	23.4	22.7	0.8	3.39	20.0	2.1	.48	.46
4f		16.4	14.6	23.0	14.5	10.29	21.5	5.8	.40	.46
3g		17.2	32.2	25.2	9.4	6.07	31.5	4.7	.38	.46
2d		18.2	16.7	28.3	4.3	2.70	34.0	2.8	.48	.47
4g		18.7	6.0	29.9	19.0	8.84	[a]		.42	.47
3h		19.4	24.2	32.1	13.3	6.00	39.4	5.3	.36	.47
2g		20.7	7.3	36.6	8.8	4.88	30.2	3.4	.37	.47
2h		21.7	3.0	40.2	12.2	4.06	[a]		.46	.47
3j		23.2	8.4	45.9	21.2	5.95	39.4	5.3	.37	.48
3k		24.3	3.5	50.4	23.7	5.80	[a]		.41	.48
4b	4050	6.1	39.2	3.2	2.2	5.70	35.7	2.2	.13	.17
3c		12.7	45.9	13.8	2.6	4.65	33.7	2.0	.19	.22
4e		13.9	22.5	16.5	10.5	7.28	40.6	4.0	.20	.23
3e		15.6	37.2	20.8	6.9	4.04	44.7	2.2	.19	.23
2c		17.2	20.2	25.2	2.4	3.95	21.8	1.6	.29	.24
2e		19.4	12.6	32.1	6.3	6.43	30.0	2.7	.22	.25
3i		21.3	16.5	38.8	17.3	6.00	55.7	4.5	.21	.25
3b	4350	12.2	47.3	12.7	1.9	15.9	60.0	−0.1	...	...
2a		15.8	25.0	21.3	0.0	13.5	10.0	+.2	...	...
3f		16.1	35.6	22.2	7.7	13.8	60.1	−.1	...	...
2f		20.0	10.0	34.2	7.5	18.4	30.2	.0	...	...

[a] These illuminations were continued until the decomposition of nitrogen pentoxide was complete. The rates given in the tenth column were obtained from the slopes of the curves plotted as in **Fig.** 2 for the interval in which nitrogen pentoxide was known to be present.

$$\frac{dp_{N_2O_5}}{dp_{\text{total}}} = -\frac{2K + 8p_{NO_2}}{3K + 4p_{NO_2}}$$

where $K = p^2_{NO_2}/p_{N_2O_4}$ and has the value 11.7 at 0° when pressures are expressed in mm. of mercury. The change in the partial pressure of N_2O_5 during an illumination was then calculated from the expression

---

[9] Schreber, *Z. physik.* Chem., **24, 651 (1897).**

$$\Delta p_{N_2O_5} = -\Delta p_{\text{total}} \frac{2K + 8p_{NO_2}}{3K + 4p_{NO_2}}$$

using the mean partial pressure of NO_2; p_{NO_2} ordinarily underwent only a small change during an illumination. In the tenth column are given the changes in $p_{N_2O_5}$ per ten minutes per cm. of galvanometer scale deflection. It will be noted that at all values of p_{NO_2}, including the larger ones at which absorption was presumably fairly complete, the radiation 3660 Å. is considerably more effective than the radiation 4050 Å. This fact, as well as the ineffectiveness of the radiation 4350 Å., is entirely accountable if the mechanism is the decomposition of NO_2 into NO and O_2 followed by a dark reaction between NO and N_2O_5; for these N_2O_5 rates closely parallel the quantum yields in the NO_2 decomposition. In order to determine whether the N_2O_5 rates have the proper absolute magnitude to be accounted for in this manner, as well as to eliminate, so far as possible, uncertainties arising from incomplete absorption and from the fact that the previous NO_2 work had been done at room temperature rather than at 0°, we have undertaken measurements of the rate of NO_2 decomposition in the same reaction vessel.

For this purpose the apparatus was sealed at C and P (Fig. 1) and a reservoir, S, containing nitrogen dioxide, was sealed on at the point indicated, as were also a trap, T, and a receptacle, R, which served as a sink for nitrogen dioxide after it had been illuminated once. Liquid air was maintained at a constant level around the trap, G, and the thermostat kept packed with ice. The nitrogen dioxide in S was kept frozen out with liquid air, out of contact with stopcock grease, except at the time of its introduction into the reaction vessel.

The method followed was to evacuate the whole system, close stopcock M, remove the liquid air from the reservoir, S, thus introducing some nitrogen dioxide into the apparatus, freeze this out in T, evacuate well, then remove the liquid air from around T with the stopcock M closed. The pressure of nitrogen dioxide and tetroxide was now measured and a measured illumination of from two to four minutes made with λ4050 or 3660. Immediately after illumination, liquid air was applied at T, the stopcock, M, opened and the pressure of oxygen read on the McLeod gage. It has been shown in the previous research that nitric oxide is frozen out along with nitrogen dioxide. The amount of decomposition was kept low enough so that the recombination of NO and O_2 could be neglected. A blank run, in which the illumination was omitted, showed the development of non-condensable gas while the NO_2 was in contact with the stopcocks to be entirely negligible.

The volume of the apparatus between the points C and C′ was found by filling with water to be 37.8 cc. In order to be able to calculate the pressure the oxygen formed would exert if it were all in this volume at

0°, air was trapped in the McLeod gage of known volume and its pressure read. In the meantime the rest of the apparatus, with liquid air and ice in place as in the oxygen measurements, was well evacuated. Then with the cock, N, closed the air was released from the McLeod gage and the pressure again read.

The rates of production of oxygen in the NO_2 experiments, expressed as millimeters per ten minutes per centimeter of scale deflection and reduced to the volume and temperature of the reaction vessel, were plotted against p_{NO_2} and a representative curve was drawn. From this curve were read the rates of oxygen production corresponding to the particular values of p_{NO_2} occurring in the N_2O_5 experiments. Twice these rates are given in the last column of Table I. The multiplication by two is made in order to permit direct comparison of the last two columns.

Discussion of Results

The last two columns of the table, which summarize the results for the wave length 3660 and 4050 Å., may be considered to agree within the experimental error. It may be noted that in Expts. 4a and 4b the ratios of $p_{N_2O_5}$ to p_{NO_2} were about 10 and 6.5, respectively. The agreement of the rate of N_2O_5 decomposition with twice the rate of O_2 production in the absence of N_2O_5 but at the same NO_2 pressure is to be expected if the N_2O_5 does not interfere with the photochemical decomposition of NO_2 ($2NO_2 = 2NO + O_2$), and if the N_2O_5 decomposition is simply a dark reaction with NO ($N_2O_5 + NO = 3NO_2$). In other words, the comparative rates in the two sets of experiments are in agreement with the N_2O_5 mechanism proposed by Norrish. The fact that the effect of $\lambda 4350$ is too small to detect with the arrangement we have used is likewise in agreement with this mechanism if consideration be taken of the low quantum yield of this radiation in decomposing NO_2.

The possibility that the N_2O_5 decomposition results from collisions of the second kind between activated NO_2 molecules and N_2O_5 molecules is not completely ruled out. But this mechanism would, in view of the present results, require very special assumptions concerning the efficiencies of these collisions as compared with the efficiencies of the collisions involved in NO_2 decomposition. However, since the efficiencies of collisions of the second kind are ordinarily highly specific with respect to the colliding molecules,[10] such assumptions could only fortuitously be in agreement with present views. The possibility that such collisions might account for a small part of the decomposition would appear to be difficult to eliminate. However, certainly the major part of the N_2O_5 decomposition which we have observed is predicted satisfactorily by the Norrish mechanism.

---

[10] Frank and Jordan, "Anregung von Quantensprungen durch Stosse," Julius Springer, Berlin, 1926, p. 225.

Summary

The photochemical decomposition of gaseous nitrogen pentoxide in the presence of nitrogen dioxide has been investigated with approximately monochromatic radiations of the wave lengths **4350, 4050** and **3660 Å.** From a comparison of the rates of photochemical decomposition of nitrogen pentoxide and nitrogen dioxide, it is concluded that the mechanism of this sensitized photochemical decomposition is essentially that suggested by Norrish, namely, the formation of nitric oxide and oxygen from the photodecomposition of nitrogen dioxide, followed by dark reaction between nitric oxide and nitrogen pentoxide.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE COLLEGE OF THE CITY OF DETROIT]

VAPOR PRESSURES OF RELATED COMPOUNDS. THE APPLICATION OF DÜHRING'S RULE

BY A. R. CARR AND D. W. MURPHY

RECEIVED AUGUST 8, 1928 PUBLISHED JANUARY 8, 1929

Several methods have been proposed to show the relation between the vapor-pressure data for various substances. The approximate Clausius-Clapeyron equation states that the slope of the vapor-pressure curve of any substance is proportional to its molal entropy of vaporization. In other words, the slopes of the vapor-pressure curves of non-associated substances at the same pressure should be the same. However, due to deviation from the gas laws and for other reasons, over wide pressure ranges this is not the case. Hildebrand[1] has suggested that this equation would be more nearly correct if the comparisons between various liquids were made at equal vapor concentrations rather than at equal pressures. Wilson and Bahlke[2] found that this method is applicable to the paraffin hydrocarbons.

Another common method, also based on the Clapeyron equation, is to plot the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Over short ranges of temperature the data for related substances give straight lines which are nearly parallel. However, as the temperature range increases, the straight lines are replaced by curves. Still other methods are empirical, such as those proposed by Ashworth[3] and Cox.[4] Calingaert and Davis[5] applied the Cox method to several groups of related substances and found that the lines representing

---

[1] Hildebrand, THIS JOURNAL, 37, 970 (1915).

[2] Wilson and Bahlke, *Ind. Eng. Chem.*, *16*, 115 (1924).

[3] Ashworth, *J. Inst. Petroleum Tech.*, 10, 787 (1924).

[4] Cox, *Ind. Eng. Chem.*, 15, 592 (1923).

[5] Calingaert and Davis, *ibid.*, 17, 1287 (1925).

the vapor-pressure data for each substance in the groups so plotted tend to intersect in a common point.

It is the purpose of this paper to show that the Diihring lines, representing the vapor-pressure data for each one of a family of substances, intersect in a common point. As will be shown, this simplifies the construction of the vapor-pressure curve for each substance in the group. Relatively few experimental determinations are required to obtain these vapor-pressure data, which are sufficiently accurate for many purposes.

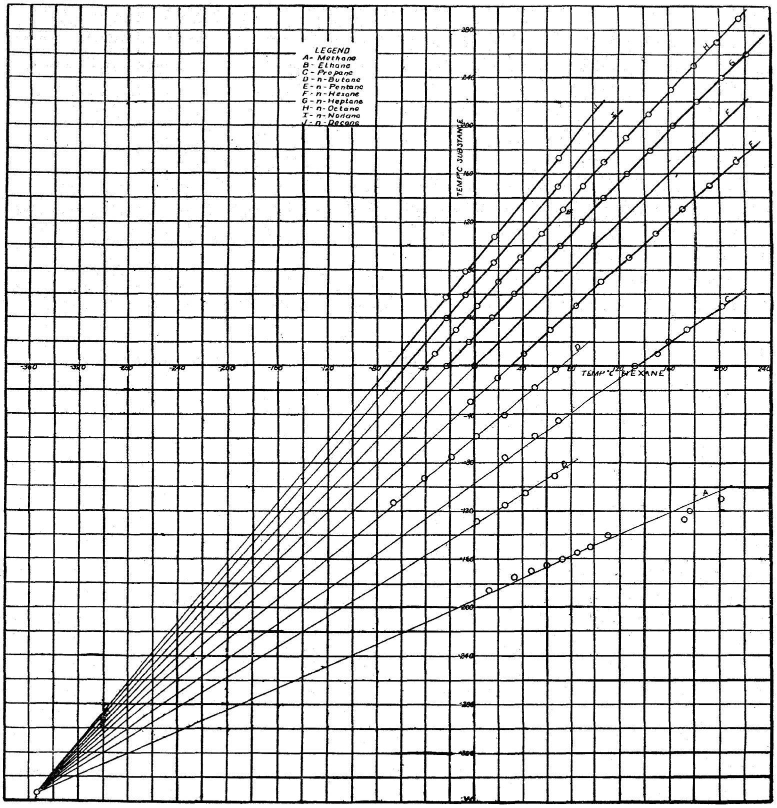


Fig. 1.

In 1878, Dühring[6] discovered a simple relation between the boiling points of pure substances. He plotted the boiling point of one substance at a given pressure as the ordinate against the boiling point of water at the same pressure as the abscissa. Repeating this process for several widely different pressures, he showed that a straight line could be drawn through all the points thus determined. This rule greatly simplifies the

---

[6] **Diihring, "Neue Grundgesetze zur Rationelle Physik und Chemie," Leipzig, 1878.**

construction of vapor-pressure curves. Once the Diihring line for the substance or compound is constructed, the pressure corresponding to any boiling point may be found in the following manner. Through any temperature representing the boiling point of the substance, draw a line parallel to the horizontal axis and intersecting the Diihring line. Through this point of intersection, draw a line parallel to the vertical axis and read the boiling point of the reference substance under the same pressure as that of the substance in question. From the vapor-pressure curve of the reference substance read the pressure corresponding to this temperature. By repeating this process for various temperatures, the vapor-pressure curve for the substance may be determined.

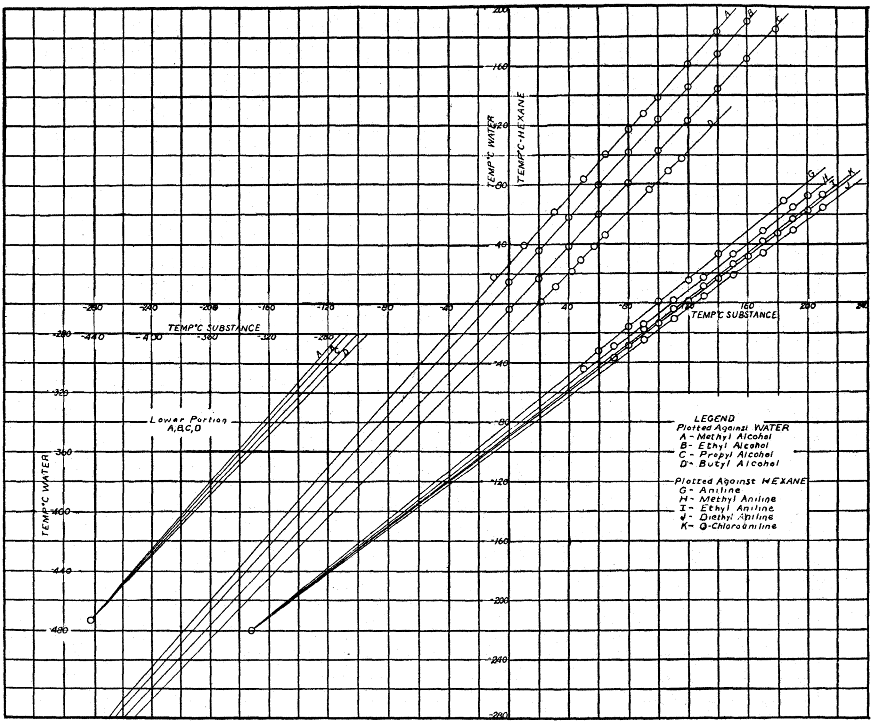


Fig. 2.

Diihring expressed his rule algebraically as follows

$$\frac{T_1 - T_2}{\Theta_1 - \Theta_2} = K$$

in which T_1 and $1'_2$ are the boiling points of one substance at two different pressures, while Θ_1 and Θ_2 are the boiling points of the other substance at the same two pressures and K is a constant which is the slope of the line. Diihring's rule has been shown to hold remarkably well for substances and compounds over pressure ranges of several thousand millimeters when the boiling points of the substance or compound in question are plotted against the known boiling points of a chemically similar substance. In general the broader the pressure range and the less similar the substances, the greater will be the deviation from a straight line.

Furthermore, it may be seen from the charts that the Diihring lines for **a** family of substances either intersect in a common point or are parallel.

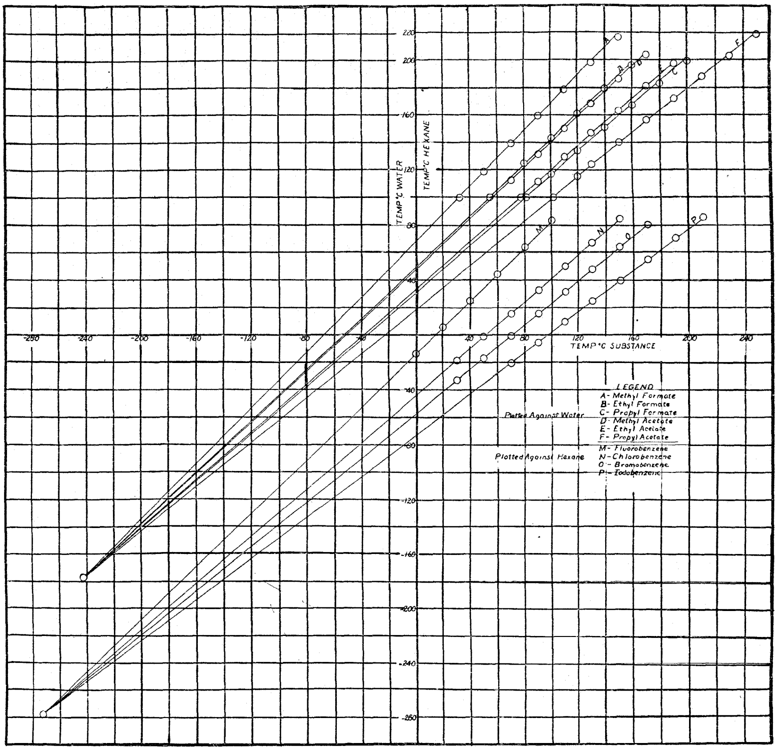


Fig. **3.**

The requirements for the construction of a Diihring chart for a family of substances are as follows: (1) the vapor pressure of some reference substance, such as water or hexane, must be accurately known and (2) at least two boiling points at different pressures of two substances in the family should be determined in order to establish the common point of intersection of the Diihring lines for the family. After this point of intersection is established, it is possible to construct the vapor-pressure curve of any member of the family of substances from a single boiling point.

Fig. 1 shows the normal paraffin hydrocarbons from methane through decane. These are plotted against normal hexane as the reference substance. The lines for most of these hydrocarbons fit the data very accurately through wide pressure ranges, but from butane down the data become somewhat discordant, with that of methane deviating most widely from a straight line. The vapor-pressure data of the reference substance, hexane, which we have used were taken from Von Rechenberg.[7] The Dühring lines for the isomers of the normal hydrocarbons, not shown in the figure, intersect in a different point from that of the normal hydrocarbons.

In Fig. 2, A, B, C and D are, respectively, methyl, ethyl, propyl and butyl alcohols plotted against water as the reference substance, while

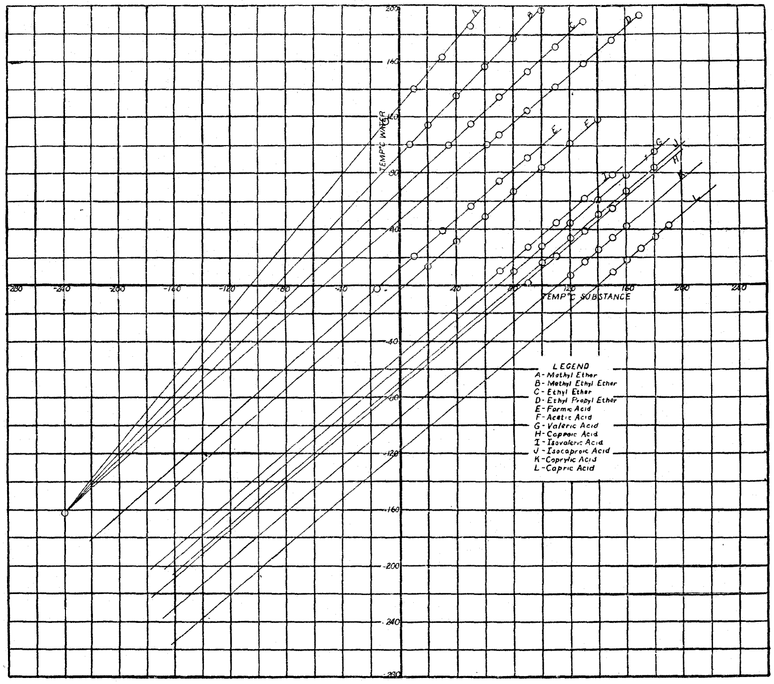


Fig. 4.

G, H, I, J and K are aniline, methylaniline, ethylaniline, diethylaniline and o-chloro-aniline, respectively, plotted against hexane. The anilines when plotted against water showed curves of similar shape, but with hexane as the reference substance they formed straight lines which intersected in a common point.

In Fig. 3, A to F inclusive are the lines for several organic esters plotted against water, while M to P inclusive are halogen derivatives of benzene plotted against hexane. Fig. 4 gives several ethers and several acids with

---

[7] Von Rechenberg, "Einfache und Fraktionierte Destillation in Theorie und Praxis," Von Schimmel and Company, Leipzig, 1923.

water in both cases as the reference substance. It is a curious fact that the Dühring lines for the various organic acids studied are parallel.

The literature does not yield complete vapor-pressure data over wide temperature ranges for many whole families of compounds. Where such data were available and were plotted against a similar substance for reference, the Dühring lines so formed were straight and intersected in a common point.

Acknowledgment

The authors wish to acknowledge the aid of Miss Elinor Batie in collecting data from the literature and in checking calculations.

Bibliography

Fig. **1.** Hydrocarbons—CH_4: Olszewski, *Compt. rend.*, 100, **940 (1885)**; Stock, Henning and Kuss, *Ber.*, **54,1119 (1919).** C_2H_4: Burrell and Robertson, THIS JOURNAL, **37,1893 (1915)**; Maass and McIntosh, *ibid.*, **36,737 (1914).** C_3H_6: Burrell and Robertson, *ibid.*, **37, 2188 (1915)**; Hainlen, *Ann.*, **282, 229 (1894).** C_4H_{10}: **Burrell and** Robertson, THIS JOURNAL, **37, 2193 (1915)**; Seibert and Burrell, *ibid.*, **37, 2691 (1915).** C_5H_{12} to C_8H_{18}: Young, *Proc. Roy. Dublin Soc.*, **12, 389 (1909).** C_9H_{20} and $C_{10}H_{22}$: Krafft, *Berl. Ber.*, 15, **1692 (1882).**

Fig. *2*. Alcohols—Young, "International Critical Tables," Vol. **3,** p. **217.** Anilines —"International Critical Tables," Vol. **3,** p. **221;** Nelson and Wales, THIS JOURNAL, 47, **867 (1925)**; Kahlbaum, **Z.** *physik. Chem.*, **26, 577 (1898).**

Fig. **3.** Ethers—Cardoso and Bruno, **J.** *chim. phys.*, **20, 347 (1923)**; Berthoud and Bruin (1862), **J.** *chim. phys., 21, 143* **(1924)**; Regnault, *Mem.*, **26, 335 (1862).** Acids—Burrell and Robertson, THIS JOURNAL, **37, 2691 (1915)**; Kahlbaum, *Z. physik. Chem.*, **13, 14 (1894)**; Drozdowski and Pietrzak, Bull. Int. *Acad. Sciences Cracovie*, **219 (1913).**

Fig. **4.** Organic esters—Young and Thomas, **J.** *Chem. Soc.*, **63, 1191 (1893).** Benzene derivatives—Mundell, *Z. physik. Chem., 85,* **435 (1913)**; Young, *Proc. Roy. Dublin Soc.*, **12, 374 (1910).**

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE RARE AND PRECIOUS METALS EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

CRITICAL STUDIES ON THE FUSION OF RARE METAL ORES. III. DETERMINATION OF TANTALUM AND COLUMBIUM[1]

BY GEORGE W. SEARS[2]

RECEIVED AUGUST 21, 1928 PUBLISHED JANUARY 8, 1929

In a previous investigation[3] it was shown that tantalum and columbium can be completely separated from each other by the action of concentrated sulfuric acid on the compounds obtained by fusion with sodium pyrosulfate at 835 to 875°C. Fusion under these conditions renders the tantalum insoluble in concentrated sulfuric acid while the columbium remains soluble. This action was explained on the basis that the sodium salts of tantalic and columbic acids are formed during the fusion and that the sodium tantalate is decomposed at 835° while the corresponding columbium compound remains unaffected at temperatures as high as 875°. The present investigation was undertaken in order to find the conditions, if possible, whereby these reactions can be applied to a quantitative determination of the two elements.

Among the available methods for the determination of tantalum and columbium, those involving the difference in solubility of the potassium double fluorides appear to be the most satisfactory. All of these[4] necessitate the fractional precipitation of tantalum as K_2TaF_7. The double fluoride is weighed as such or is converted to the oxide and weighed as Ta_2O_5. The columbium remaining in the solution is usually converted to the oxide and weighed as Cb_2O_5, although it may be determined volumetrically by reduction and subsequent oxidation with standard potassium permanganate. Titanium, which usually occurs with tantalum and columbium, is not removed by the double fluoride method and is weighed with the columbium. Its estimation colorimetrically with hydrogen peroxide has been found by Chesneau[4] to involve an error of at least 0.5%. Treadwell,[5] and also Schoeller and Waterhouse,[6] investigated the methods of reducing columbium and found that in no case could it be reduced to the tervalent state and that the degree of reduction varied so much with conditions that

---

[1] Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Consulting Chemist, U. S. Bureau of Mines. Professor of Chemistry, and head of Department of Chemistry, University of Nevada.

[3] Geo. W. Sears, THIS JOURNAL, 48, 343 (1926).

[4] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry," MacMillan Co., London, 1913, Vol. II, p. 955; W. B. Giles, *Chem. News*, **99**, 1, 25 (1909); E. S. Simpson, *ibid.*, 99, 243 (1909); G. Chesneau, *Compt. rend.*, 149, 1132 (1909); E. Meimberg, *Z. angew. Chem.*, 26, **83** (1913).

[5] W. D. Treadwell, *Helv. Chim. Acta*, 5, 806 (1922): *C. A.*, 17, 505 (1923).

[6] W. R. Schoeller and E. F. Waterhouse, *Analyst*, **49**, 215–220 (1924).

a definite factor was not possible. The method was therefore declared unsatisfactory. Schoeller and Powell[7] attempted a separation and determination by fusing with potassium carbonate. The greater solubility of the columbium compound afforded a fairly complete separation after two or three fusions. Interfering elements, however, make the method unreliable for the determination of tantalum.

It may be concluded, therefore, that the present methods for the determination of tantalum and columbium involve fractionation processes which are at best only approximate. Interfering elements are very difficult to remove and hence often contaminate the precipitated tantalum and columbium. Iron and titanium, almost universally found associated with tantalum and columbium, are among the most troublesome and most difficult elements to remove.

Experimental Part

Since titanium sulfate, formed by fusion with sodium pyrosulfate below 700°C., is soluble in hot 3 N hydrochloric acid[8] and both tantalic and columbic acids are known to be relatively insoluble in water and dilute mineral acids, fusion of the ore or mixed oxides with sodium pyrosulfate should offer a possible means of separating any titanium that might be present. Iron and other more basic elements should also be soluble under these conditions.

Solubility of Tantalic and Columbic Acids in Dilute Hydrochloric Acid.—Tantalic and columbic acids were obtained by fusing the mixed oxides with sodium pyrosulfate and leaching the cold melt with water This procedure dissolved a large proportion of the excess sodium sulfate and left all the tantalum and columbium as a fine granular or flocculent residue, the density of which depended somewhat on the temperature at which the fusion was made. The residue was allowed to settle and the liquid decanted through a filter. Three normal hydrochloric acid was then added to the residue remaining in the beaker and the mixture was digested near the boiling temperature for some time. It was then filtered and the filtrate evaporated to a few cubic centimeters and tested for columbium according to the method outlined in the previous paper.[3] Several experiments were carried out in this way on mixtures that had been fused at different temperatures. In no case was even a trace of columbium detected. Although the tests for tantalum are somewhat less satisfactory than for columbium, tests were made by adding hydrofluoric acid and potassium chloride to the concentrated filtrate, allowing excess water to evaporate, and examining the residue under the microscope for the needle-like crystals of K_2TaF_7. No evidence of tantalum was obtained in any case. It was therefore assumed that no loss of either tantalum or columbium would result from washing with hot 3 N hydrochloric acid.

Removal of Contaminating Substances.—From the difficulties encountered a number of years ago in washing large quantities of tantalic and columbic acids free from potassium sulfate it seemed probable that similar difficulties might arise in the removal of the sodium sulfate obtained during the fusion. Accordingly a number of samples of the mixed oxides were

---

[7] W. R. Schoeller and A. R. Powell, *J. Chem. Soc.*, **119**, 1927 (1921).

[8] George W. Sears and Laurence Quill, THIS JOURNAL, 47, 922 (1925).

fused with sodium pyrosulfate, the cold melt was leached with water and the residue washed with hot 3 N hydrochloric acid. By repeated digestion in the hot wash liquid it was found that no further test for sulfate could be obtained after six or seven washings if the sample taken for analysis was less than half a gram. Larger samples were much more difficult to wash free from sulfate. In order to determine whether sodium sulfate might be occluded in such a way as to prevent its being washed out, two samples of pure potassium fluotantalate were fumed with sulfuric acid to remove the fluorine and then analyzed for tantalum oxide as described above. The results are given in Table I.

TABLE I

DETERMINATION OF Ta_2O_5 IN K_2TaF_7

K_2TaF_7 taken, g.	Ta_2O_5 found, g.	Ta_2O_5 present, g.	Error, g.
0.6227	0.3520	0.3512	+0.0008
.5180	.3914	.3917	− .0003

The removal of iron presented a somewhat greater difficulty. The iron compound obtained during the fusion appeared to be almost completely insoluble in water, regardless of whether the fusion was made at a low or high temperature. Repeated digestion with hot 3 N hydrochloric acid proved efficient for removing the iron when the fusion was carried out at a low temperature. High-temperature fusions, however, appeared to decompose the iron compound or otherwise render it very difficultly soluble in the dilute acid. By fusing at a low temperature (about 650°) and leaching the cold melt with water to remove it from the crucible, much of the excess sodium sulfate was dissolved and the tantalum and columbium were left as a fine, white, granular residue that settled readily. All iron and sodium sulfate could be removed from the residue by repeated digestion with hot 3 N hydrochloric acid and final washing with water. When the insoluble residue of tantalic and columbic acids which had been washed until the washings gave no further test for iron or sulfate was filtered, dried and ignited, a pure white powder was obtained.

The results so far obtained, together with the fact that the fusion of titanium ores below 700° renders the titanium completely soluble[8] in hot 3 N hydrochloric acid, made it seem quite probable that titanium could be quantitatively removed along with the iron. In order to test this point a sample of pure tantalum oxide, to which was added a small amount of titanium oxide, was fused with the pyrosulfate at about 650° and analyzed as described above. The final washing with hot 3 N hydrochloric acid was continued until no further test for titanium was obtained in the washing liquid when tested with hydrogen peroxide. A portion of the residue was then fused and tested for titanium and gave a negative result. It was evident, therefore, that the chief interfering substances could be removed by fusing at about 650°, washing first with hot 3 N hydrochloric acid and then with water.

Separation of Tantalum and Columbium

In order to effect a separation between the tantalum and columbium by means of the pyrosulfate fusion the temperature of the fusion mixture must reach 835 to 875°. In the earlier investigation[3] fusions were made in platinum over a Bunsen flame and the temperatures were obtained by means of a thermocouple placed in the fused mass. Since this procedure was not feasible for a quantitative determination, it was decided to use an electric resistance cup furnace as the source of heat. The thermocouple was suspended just above the crucible containing the melt. A number of experiments were carried out in order to determine the furnace temperature and the rate of heating necessary to decompose completely the tantalate without affecting the columbate. It was soon found that time is a factor in the decomposition of the tantalate. This fact did not appear in the earlier investigation, probably because the temperature had to be raised much more slowly in order to prevent boiling when the flame was used as the source of heat. A satisfactory separation was found possible if the temperature was held at 835 to 850° for ten to fifteen minutes.

Determination of Total Tantalum and Columbium

For the purpose of a quantitative determination of the two elements by this method, a filter medium unaffected by the hot concentrated sulfuric acid would be necessary. A Gooch crucible provided with an asbestos pad seemed to be the most logical substance available; hence a quantity of the washed asbestos fiber commonly used in quantitative analysis was heated with concentrated sulfuric acid for two to three hours and then carefully washed with water to remove the sulfuric acid and any other soluble material that might have been present. A suspension of this was made in the usual way and used in a series of determinations made with pure potassium fluotantalate. The procedure consisted in converting a weighed quantity of the fluotantalate to the oxide by fuming with sulfuric acid in a platinum crucible, evaporating the excess sulfuric acid and fusing the residue with twelve parts of sodium pyrosulfate at about 850". The cold melt was then leached with water to remove it from the crucible and dissolve as much of the sodium sulfate as possible. It was then filtered through a Gooch crucible provided with an asbestos pad, the dry weight of which had previously been determined.

The residue of tantalic acid was washed with hot 3 N hydrochloric acid and finally with water until no further test for sulfate could be obtained in the washings. The residue of tantalic acid together with the asbestos pad was transferred to the original beaker with as little water as possible and 10 to 15 cc. of concentrated sulfuric acid was added. The resulting mixture was carefully evaporated until dense white fumes of sulfur trioxide appeared, and was then held at that temperature for about ten minutes. When cold the mixture was filtered through a weighed Gooch crucible, washed, dried, ignited and weighed.

The results were irregular, showing some unexpected interfering factor. It seemed, therefore, that the asbestos was being attacked by the sulfuric acid. In order to determine to what extent this was being done, a weighed quantity of the asbestos was subjected to the action of hot concentrated sulfuric acid in a manner similar to that required by the analysis. Several determinations of this kind showed a small but distinct loss of weight during the treatment. A number of alundum filtering crucibles were tested in a similar manner, but they were found to be much less resistant than the asbestos. The solvent action of hot concentrated sulfuric acid on platinum indicated that a Monroe crucible would be little better for this purpose than the ordinary Gooch. From these results it seemed doubtful whether a material entirely resistant to the action of the hot acid could be found.

Two possible methods of procedure presented themselves. A correction might be made for the asbestos dissolved during the treatment with sulfuric acid or the weight of tantalum oxide could be obtained by difference. Investigation of these two methods was carried out in the following manner, using a mixture of the oxides of tantalum and columbium containing a small amount of iron oxide. From 0.2 to 0.3 g. of the mixed oxides was weighed in a platinum crucible, 4.5 to 5.0 g. of sodium pyrosulfate added and the mixture fused over a Bunsen flame at as low a temperature as possible to obtain a clear fusion. By keeping the crucible covered and the flame just high enough to keep the mass liquid but not boiling, a satisfactory fusion could be obtained in about forty-five minutes to an hour. The crucible containing the cold melt was placed in a beaker containing enough water to cover it and was allowed to stand for one to two hours, when the undissolved residue was disintegrated and easily removed from the crucible. After thorough mixing the residue was allowed to settle and the liquid was decanted through a filter. A small quantity of 3 N hydrochloric acid was then added and the mixture digested near the boiling temperature for 10 to 15 minutes. This served to dissolve most of the iron, which was decanted through the same filter. By repeating this process three to four times no further test for iron could be obtained in the washings. Several washings with hot water were required to remove all the sulfate. The residue was then transferred quantitatively to the filter, dried, ignited and weighed. In all cases the ignited residue was pure white, indicating the absence of iron. A small portion held in the flame by means of a platinum wire gave no yellow color, showing the absence of sodium. A small amount of silica, however, was found to be present. This was removed by treatment with hydrofluoric and sulfuric acids. The final residue was assumed to be the pure oxides of tantalum and columbium. Consecutive analyses gave results calculated in per cent. as follows: 98.00, 98.20, 98.11, 97.97, 98.04; average, 98.06.

Separation and Determination of Columbium

For the separation and determination of columbium the pure oxides obtained by the above method were fused as before over a Bunsen flame. When the fusion was complete and a clear liquid resulted, the crucible and contents were placed in the furnace, the temperature was brought to 850° and maintained at approximately that temperature for ten to fifteen minutes. At the end of this time they were removed from the furnace and allowed to cool. Fumes of sulfur trioxide ceased to be evolved sometime before the temperature of the furnace reached 850°, and the mass solidified. When taken from the furnace it was quite porous and had a flaky appearance. This was most easily removed from the crucible by digesting for one to two hours with water kept near the boiling temperature. A small portion, however, clung very tenaciously to the crucible. It was found impossible to remove this except by fusing again with the pyrosulfate at a low temperature. Since this would necessarily introduce an error into the determination, some container other than a platinum crucible would be necessary for the high-temperature fusion. A silica crucible not being available at the time, a Coors glazed porcelain crucible was tried. The results were very satisfactory. Not only was the fused mass very easily and completely removed from the crucibles but the loss in weight caused by the fusion was very much less than that sustained by the platinum. In five fusions two porcelain crucibles lost a total of 3.0 and 2.3 mg., respectively, while a platinum crucible similarly treated lost 7.7 mg. Porcelain was therefore used for all high-temperature fusions thereafter. The cold melt was leached with water and washed with two or three portions of hot 3 N hydrochloric acid to remove any iron that might have been introduced with the pyrosulfate, decanting each time through a Gooch crucible provided with an asbestos pad.

The residue of tantalic and columbic acids, together with the asbestos pad, was then transferred to the original beaker with the aid of as little water as possible, and 15 cc. of concentrated sulfuric acid was added. The mixture was evaporated until the white fumes of sulfur trioxide appeared. The beaker was then covered with a watch glass and the heating continued for twelve to fifteen minutes; this served to dissolve all of the columbium without affecting the tantalum. On cooling, it was filtered through a weighed Gooch crucible, washed with two or three portions of cold 6 *N* sulfuric acid,[3] and then with water until the washings gave no further precipitate with ammonia.

A good deal of difficulty was encountered in this filtration owing to the fact that the finely divided tantalum residue tended to pass through the filter. After the sulfuric acid treatment the tantalum is left as a dense, granular mass, some of which is very finely divided. A small amount may pass into the filtrate and entirely escape notice since it appears to give little or no cloudiness to the concentrated acid solution. Until its presence was suspected and the solution carefully examined for it, a good many unaccountably high columbium values were obtained.

On diluting the filtrate containing the columbium it was noticed that in most cases a distinct cloudiness developed, indicating hydrolysis, although in some cases the solution remained perfectly clear. It seemed probable, therefore, that the concentrated acid solution might be diluted without fear of hydrolysis if the correct conditions could be found. After some investigation it was found that no hydrolysis occurred and that a complete separation could be obtained if the cold acid solution were slowly poured, with constant stirring, into about 100 cc. of water kept cold with ice or running water.[9] This simplified very much the process of filtering and washing the residue free from columbium.

---

[9] After this work was completed and the paper had been sent to Washington, an article by S. J. Kiehl and David Hart, appeared (THIS JOURNAL, 50, 1608 (1928)) describing a similar method for diluting a sulfuric acid solution of columbic oxide without causing precipitation.

The most favorable conditions found for the precipitation and separation of columbium were to neutralize the solution, which had been diluted to about 300 cc., with ammonia and then heat to boiling. This caused the precipitate to settle well and make it more easily washed. A number of attempts were made to precipitate the columbium by means of hydrolysis in acid solution but conditions could not be obtained under which complete precipitation could be assured. The precipitate of columbium usually contained a small amount of silica, which was removed by treatment with hydrofluoric and sulfuric acids. Consecutive analyses gave results calculated in per cent. as follows: 21.90, 21.86, 22.42; average, 22.06.

Attempts to obtain the weight of the tantalum oxide by igniting and weighing the residue did not meet with success. The correction for the asbestos which had to be placed in the hot concentrated sulfuric acid apparently was not constant in value and could not be obtained for each determination.

Method of Analysis

The procedure finally adopted as giving the most satisfactory results consisted in fusing the weighed sample at about 650° with 12 to 13 parts of sodium pyrosulfate and leaching the cold melt with water to remove it from the crucible and dissolve most of the excess sodium sulfate. The clear supernatant liquid is then decanted through a filter, the residue digested with hot 3 N hydrochloric acid to remove iron and titanium, transferred to the filter, washed free from sulfate with hot water, dried and ignited. This product contains all of the tantalum and columbium along with a small amount of silica, which is removed by treatment with hydrofluoric and sulfuric acids. After weighing the pure mixed oxides, a definite portion is transferred to a porcelain crucible and fused in the furnace with 5 g. of sodium pyrosulfate. The temperature is slowly raised to 850° and held at 835 to 850° for ten to fifteen minutes. It is then removed from the furnace, leached with water, filtered through a Gooch crucible, provided with an asbestos pad and washed two or three times with hot 3 N hydrochloric acid. The residue, together with the asbestos pad, is then transferred to the original beaker, with the aid of as little water as possible, and 15 cc. of concentrated sulfuric acid is added. The mixture is then evaporated to the appearance of white fumes and kept at that temperature for ten to fifteen minutes with occasional stirring. When cold the concentrated acid solution is slowly poured with constant stirring into 100 cc. of water kept cold with ice or running water. The mixture is then filtered, washed with cold water, and the columbic acid precipitated from the filtrate with ammonia. The precipitate is filtered, dried, ignited, and the silica removed by treatment with hydrofluoric and sulfuric acids. The final residue is weighed as Cb_2O_5.

Summary and Conclusion

The pyrosulfate fusion as a means for the quantitative determination of tantalum and columbium has been studied with results and conclusions as follows.

1. When fused at a low temperature (about 650°) iron and titanium are completely separated from the tantalum by digestion near the boiling temperature with 3 N hydrochloric acid. The tantalic and columbic acids are left in the insoluble portion.

2. When the fusion mixture is held at 835 to 850° for ten to fifteen minutes, the columbium only is dissolved by fuming with concentrated sulfuric acid. The solution may be diluted without precipitation if the cold acid mixture is slowly poured into water kept cold with ice or running water.

3, A method of procedure for the determination of tantalum and columbium is given.

4. The possibility of more economic extraction and separation of tantalum and columbium is indicated in the method used for the removal of iron and titanium and in the fact that the sulfuric acid solution may be diluted without precipitation of columbium.

RENO, NEVADA

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE EQUILIBRIUM BETWEEN METHANOL, CARBON MONOXIDE AND HYDROGEN. PRELIMINARY PAPER[1]

BY DAVID F. SMITH[2] AND BRIANT F. BRANTING[3]

RECEIVED AUGUST 27, 1928 PUBLISHED JANUARY 8.1929

Introduction

Although our work on the equilibrium between methanol, carbon monoxide and hydrogen is still in progress, it has been decided to present the results so far obtained. The results heretofore available are very conflicting and no direct experimental measurements of equilibrium appear to have been made. The many inquiries which have been received concerning the data indicate the general interest and practical importance attached to the thermodynamic properties of methanol.

Published values of the free energy of methanol have been obtained in several ways. Kelley[4] has calculated his value from the specific heat of

---

[1] Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Presented before the Division of Gas and Fuel Chemistry at the 75th meeting of the American Chemical Society, St. Louis, Missouri, April 17, 1928.

[2] Physical Chemist, Pittsburgh Experiment Station.

[3] Junior Inorganic Chemist, Pittsburgh Experiment Station.

[4] Kelley, *Ind. Eng. Chem.*, 18, 78(1926).

liquid methanol down to liquid-air temperatures, extrapolating to 0°K. and using the Third Law of Thermodynamics. Christiansen[5] has used a Nernst approximation formula, and also his preliminary measurements of equilibria in the two sections $HCOOCH_3 + 2H_2 = 2CH_3OH$ and $CH_3OH + CO = HCOOCH_3$. The calculation of Smith[6] involved substantially the same data that were used by Kelley, except for the substitution of a better value for the high temperature specific heat of methanol vapor. The data of Kelley were at that time considered more reliable than those of Christiansen, partly because of the latter's own statements regarding the preliminary nature of his equilibrium measurements. While the calculations of Kelley and of Smith were in substantial agreement, they were widely different from Christiansen's results. Although not much confidence can usually be placed in the results from the Nernst approximation formula, the formula as presented by Christiansen gave results in fair agreement with his equilibrium measurements.

The equilibrium constant $(CH_3OH)/(CO)(H_2)^2$, where concentrations are expressed in terms of the partial pressures in atmospheres, is 10.6 at 200° according to Smith's calculation from Kelley's data. Christiansen's equilibrium data[7] give 0.055 at this temperature. The Nernst approximation formula, as proposed by Christiansen, gives 0.042. Recently Morgan, Taylor and Hedley[8] have discussed the results of the Nernst formula which Audibert and Raineau[9] state to be in substantial agreement with the results they obtained in practical operation at high pressures. They note that the discrepancy between the results obtained from this formula and from the equation derived by Kelley increases with increasing temperature. At 600°K. the formula gives a constant about one-hundredth of that calculated from Kelley's results.

Apparently, apart from the preliminary equilibrium measurements of Christiansen, the only direct experimental estimates of the methanol equilibrium have been obtained from results of actual operation of the methanol process at high pressures—operations which were of course neither designed for nor well adapted to furnishing accurate equilibrium data. In addition to the inherent difficulties in precise measurement at high pressures, the theoretical accuracy obtainable on measurements of this equilibrium at high pressure is unsatisfactory; for example, a relatively small error in determination of the conversion of carbon monoxide to methanol would, at very high pressures, introduce a disproportionately large error into the value of the equilibrium constant so derived. Of

---

[5] Christiansen, J. *Chem. Soc.*, 128,413 (1926).

[6] Smith, *Ind. Eng. Chem.*, 19, *801* (1927).

[7] Christiansen in his paper evidently expresses concentrations in moles per liter and uses the reciprocal of the constant used here.

[8] Morgan, Taylor and Hedley, **J.** *Soc. Chem. Ind.*, **47,** 117T (1928).

[9] Audibert and Raineau, *Ann. Office Combustibles Liquides,* 1927, **Part** *4.*

course, standard free energy data cannot be obtained from equilibrium measurements at high pressures without a much more complete knowledge of the equations of state of the separate gases, both in the pure state and in the mixtures, than is at present available. Also, when a considerable amount of reaction is taking place on the catalyst, the temperature control is likely to be poor. In view of the importance of this reaction, the conflicting nature of the existing equilibrium data makes a direct determination of the standard free energy of methanol highly desirable

Experimental Procedure

At 300° and a total pressure of 1 atmosphere, Kelley's data would give the limiting (equilibrium) decomposition of methanol to CO and $2H_2$ as about 96.4%. With an active catalyst, therefore, it should be possible under these conditions to determine the limiting decomposition of methanol vapor and, under the same conditions, to determine readily the maximum yield of methanol from mixtures of carbon monoxide and hydrogen.

Our method was first to pass pure methanol vapor over an active catalyst at a rate slow enough to give substantially equilibrium conditions. This set a maximum value on the constant of the reaction. Second, a mixture of carbon monoxide and hydrogen was passed over the catalysts at a rate slow enough to give the maximum yield of methanol. The latter experiment set a minimum limit on the value of the constant.

The methanol used was made from the commercial "absolute" product which we freed from aldehydes, ketones and water according to the method described by Danner and Hildebrand[10] for ethyl alcohol. One catalyst used was zinc oxide made from pure, freshly precipitated carbonate. Another catalyst was made by adding chromic acid to purified zinc oxide, in the atomic proportions 4Zn:1Cr.[11] About 600 cc. of 8-mesh per inch catalyst was used in each experiment. The $CO-H_2$ mixture was made by adding electrolytic hydrogen from a cylinder to water gas generated by a small generator available at this Laboratory. The gas mixture was pumped from a 7-cu.m. gas holder through a liquid-air cooled trap to remove sulfur compounds and all heavy gases, over heated copper to remove oxygen and into a high-pressure cylinder.

In our early decomposition experiments, when we were guided by the data of Kelley, methanol vapor at 1 atm. pressure was passed over the catalyst. It was soon found, however, that the final concentration of methanol resulting after passage over the catalyst, even at very slow rates, not only was much smaller than was expected, but was always much larger than the maximum yield of methanol from the $CO-H_2$ mixture. It was decided that this was due either to some adsorption effect on the catalyst or to the fact that the mechanism of the reaction changes to a higher order at very low pressures of methanol. The reaction should obviously be started at somewhere near equal distance from equilibrium in the decom-

---

[10] Danner and Hildebrand, THIS JOURNAL, 44, 2824 (1922).

[11] See Smith and Hawk, J. Phys. *Chem.*, 32, 415 (1928), for method of catalyst preparation.

position and in the synthesis experiments. We therefore introduced methanol vapor into the CO–H_2 mixture by passing the latter through a saturator containing purified methanol at the temperature of a liquid ammonia bath (–38°). The vapor pressure of methanol at this temperature was still over 40 times the equilibrium pressure, so that the experiments were thus started definitely on the methanol side of equilibrium.

Fig. 1 shows the apparatus used. The gas from the cylinder, previously purified, passes into the apparatus at *a*. The flow of gas is adjusted by the head in a tube of water, *b*. The gas then passes through heated platinized asbestos in *c* to remove oxygen, then through a liquid-air trap, *d*, to remove all heavy gases, through the methanol saturator, *e*, surrounded by a bath of liquid ammonia, through the first catalyst tube, *f*, and through a liquid-air trap, *g*, to condense the remaining methanol. The gas then passes through a second catalyst tube, h, and the yield of methanol is caught in a second liquid-air trap, *i*. The gas emerging from the apparatus is passed through a flow meter, j, and a carefully calibrated meter,[12] k, in order to determine its volume. Samples of the gas after passage over each catalyst were collected and carefully analyzed to determine the partial pressures of carbon monoxide and of hydrogen with which the methanol came to equilibrium.

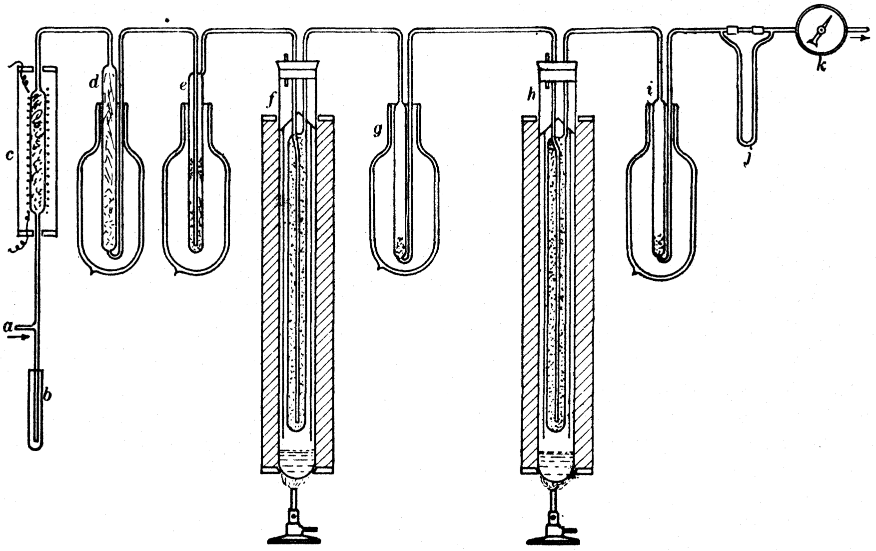


Fig. 1.—Apparatus for measuring equilibrium in the methanol reaction.

The catalyst was maintained at a constant temperature by surrounding it with the vapor of boiling benzophenone. The catalyst tubes were shielded with thin sheet-iron tubes and umbrellas, as recommended by the Bureau of Standards.[13] The benzophenone was purified by distillation before use and the boiling temperature was checked with a carefully calibrated resistance thermometer.

---

[12] In regard to calibration and use of wet-test meters, see Bureau of Standards Circular No. 309 (1926), and Technologic Paper No. 36 (1926).

[13] Bureau of Standards Scientific Paper, No. 339 (1919).

At the beginning of an experiment, in order to bring the catalyst to equilibrium with the gas mixture used, the apparatus was always completely purged with the gas to be used, before the yields of methanol were collected.

The methanol yields were determined colorimetrically, according to a method which suggested itself to us from the work of Wright.[14] The method depends upon oxidation of the methanol to formaldehyde with permanganate. The excess of permanganate is destroyed by oxalic acid, and the color is developed upon the addition of a modified Schiff's reagent, prepared as described by Wright, which forms a blue compound with the formaldehyde. It was determined that no detectable amounts of formaldehyde were formed directly by the catalyst, and that other alcohols and dimethyl ether[15] do not interfere with the test in this case. Since no other known by-products of the methanol reaction which could have been present in the solution used for the methanol determination would have interfered, the method may be regarded as an absolute determination of the methanol. Careful checks were made upon several series of known solutions and it was shown that by the colorimetric method the concentration of methanol in aqueous solutions as dilute as 1 part in 10,000 could be determined with an accuracy of 1% or better. In each determination a series of standard solutions was made up and treated in exactly the same way as the unknown solution. A calibration curve of intensity of transmitted light against the concentration of solution was plotted for interpolation purposes and the unknown solutions were always compared with a standard solution whose concentration was very close to that of the unknown solution. Since the colors were compared in a colorimeter by transmitted light, the curve of concentration against intensity was approximately logarithmic, as given by Beer's Law. Although it took a short time for the color to develop (and the color, of course, faded upon long standing), a comparison of the color in a standard solution with that in the unknown solution after each had stood for forty-five to sixty minutes gave the same result as did a comparison made an hour or more later.

The condensers containing the yields of methanol, after removal from the apparatus, were maintained at about 1° above the temperature of carbon dioxide snow until the small amount of carbon dioxide which is formed in the reaction and subsequently condensed, had evaporated from the condenser. At this temperature the vapor pressure of methanol is so low that no appreciable quantity of it could be lost. Also, there was always water present from the reaction in amount comparable to that of

---

[14] Wright, *Ind. Eng. Chem.*, *19,* 750 (1927).

[15] McKee and Burke [*Ind. Eng. Chem.*, *15,*788 (1923)] were able to determine the equilibrium between methanol and dimethyl ether using an Al_2O_3 catalyst at 350°; and Smith and Hawk [*J. Phys. Chem.*, 32,415 (1928)] showed that dimethyl ether is probably formed from methanol vapor at 1 atm. on chromium oxide catalysts. However, it is known that zinc oxide probably would give no appreciable quantities of ether at 300° [Adkins and Perkins, *J. Phys. Chem.*, 32, *221* (1928)]. Probably zinc oxide–chromium oxide catalysts which contain excess of zinc oxide would be relatively inactive also. If, as would be supposed in the absence of complete experimental information, the formation of the ether from methanol is a higher order reaction than is the formation of CO and H_2 from methanol, the rate of formation of ether from methanol at very low pressures would be negligible compared to the rate of formation of CO and H_2. Furthermore, dimethyl ether if it had been present would doubtless have disappeared during the removal of CO_2 from our condensed product as described below. At any rate, we showed by actual tests that dimethyl ether does not enter into the reaction we used to determine methanol. (Since this test for methanol is so sensitive, it is of course necessary to assure that the dimethyl ether used in the test does not contain traces of methanol.)

the methanol. Exactly 5 cc. of water was introduced into the condenser, which was then sealed, allowed to come to room temperature and shaken to dissolve the methanol into a uniform solution. The methanol in aliquot portions of these solutions was then determined, as described above.

Experiments showed that, with the type of liquid-air cooled receiver used, no methanol escaped even at much higher rates of gas flow than we had ever used in equilibrium measurements.

Since it soon became evident that the equilibrium decomposition of methanol at 304.4" was relatively far more than the expected 96.4%, it was necessary when working at atmospheric pressure to deal with rather small quantities of methanol. In spite of this, however, it was thought better to work at atmospheric pressure for the reasons mentioned and since the small quantities of methanol could nevertheless be determined accurately.

Experimental Results

The experimental results are presented in Tables I and II. In a single experiment a total gas volume of from 17 to 30 liters was passed over the catalyst. The methanol yields in Table I have been corrected, on the basis of the gas composition as given in Table II, for the volume of carbon dioxide caught in the liquid-air condensers. These yields are thus those which would be obtained from 1 cubic meter of a gas having the composition given in Table II. The analyses of the gas from different experiments were, within the limits of the error in gas analysis, not significantly different. We have thus preferred to use an average gas composition throughout. An uncertainty in the values of the equilibrium constants results from the gas analysis. The best results obtainable with this gas, using any standard method of gas analysis, may be uncertain to about 1% of the amount of carbon monoxide and about 0.5% of the amount of hydrogen. In the product $(CO)(H_2)^2$, and thus in the equilib-

TABLE I

RESULTS OF EQUILIBRIUM MEASUREMENTS

Expt. *no.*	*Synth. or decompn.*	**Av. barom. atm.**	*Temp. of catalyst,* °C.	*Rate* of **gas flow, cc./min.**	CH_3OH, g./ *cu. m. of gas* at STP	$CH_3OH/(CO)(H_2)^2$	I
1	s	0.967	303.9	9.0	0.0456	3.73×10^{-4}	−53.62
2	s	.963	303.8	4.0	.0505	4.19×10^{-4}	−53.85
3	s	.974	304.3	1.8	.0562	4.27×10^{-4}	−53.92
4	s	.966	303.9	1.6	.0520	4.27×10^{-4}	−53.89
4a	d	.966	303.9	1.6	.0767	6.30×10^{-4}	−54.66
5	s	.968	304.0	1.7	.0681	5.56×10^{-4}	−54.42
5a	d	.968	304.0	1.7	.0695	5.67×10^{-4}	−54.46
6	s	.963	303.8	1.7	.0672	5.57×10^{-4}	−54.41
6a	d	.963	303.8	1.7	.0672	5.57×10^{-4}	−54.41

TABLE II

AVERAGE ANALYSIS OF GAS

Constituent	H_2	CO	CO_2	CH_4	N_2
Volume, %	56.7	29.4	0.6	1.9	11.4

rium constant, there may be introduced in this way an error of about 2%. Further, since the ordinary wet-test meter was used to measure the total gas volumes, an error of 2% or so may also be introduced on account of change in the vapor pressure of the water and change in level of the water in the meter with variations in the room temperature during the course of an experiment—about one week. The calibration of the meter was made at the rates of gas flow used in the equilibrium measurements and in a room where the temperature was usually nearly constant. Of course, there is also an error involved in assuming that all three gases obey the perfect gas law from room temperature to 300°. However, this error is doubtless inconsiderable. In further work it is planned to eliminate these uncertainties by constructing a special gas-analysis apparatus and using a better means of measuring the gas volumes.

It was found that evacuation of the catalysts, between experiments, considerably improved their activity, probably on account of the removal of the small amounts of carbon dioxide and water adsorbed during the reaction. The promoted catalyst did not seem to be as much affected by adsorbed carbon dioxide and water as did the pure zinc oxide catalyst. It is thought that since the catalyst used in experiment 5a was pure zinc oxide that had not recently been evacuated, the constant from this experiment is somewhat high. The last two pairs of experiments (Nos. 5 and 5a, 6 and 6a) were performed most carefully and obviously came closest to equilibrium. As the best value of K we take that from Expts. Nos. 6 and 6a—namely, 5.57×10^{-4} at 303.8°.

Although the rates of gas flow were very low, and perhaps in many cases unnecessarily so, the linear rate of gas flow through the small diameter tubing connecting the various units in the apparatus was great enough to avoid possible complications due to self-diffusion of the gases.

The values, in the last column of Table I, of the integration constant, I, of the free energy equation were obtained through use of the best available heat data as given by Smith.[16] The equation expressing the free energy change in the reaction $CO + 2H_2 = CH_3OH$ is, then, $\Delta F = -20{,}857 + 41.17T \log T - 0.01423T^2 - 54.42T$. The heat data would seem to be reliable, although they have been questioned.[8] This equation gives the standard free-energy change for this reaction as 16,070 cal. at 700° K., which may be compared with the value 8930 cal. used by Lewis and Frolich[17] in their paper giving the practical yields obtained in the methanol process. Our data give $K = 6.51 \times 10^{-4}$ at 300°; the equation given by Audibert and Raineau gives $K = 11.3 \times 10^{-4}$; Christiansen's data give 4.27×10^{-4}; and Kelley's data give 8.2×10^{-2}. If Audibert and Raineau's equation was derived from their work at high pressures and the

[16] Smith, *Ind. Eng. Chem.*, 19,801 (1927).

[17] Lewis and Frolich, *Ind. Eng. Chem.*, 20,285 (1928).

equilibrium constants calculated without the use of fugacities, their constants would come out too high. Christiansen's data are fairly close to ours. However, the difference between our data and the values calculated from Kelley's data is unaccountably large. Various possible explanations for this discrepancy have been considered, but so far no satisfactory explanation can be given. In further work we hope to obtain the equilibrium constant more accurately and at several temperatures and thus throw some light on the question.

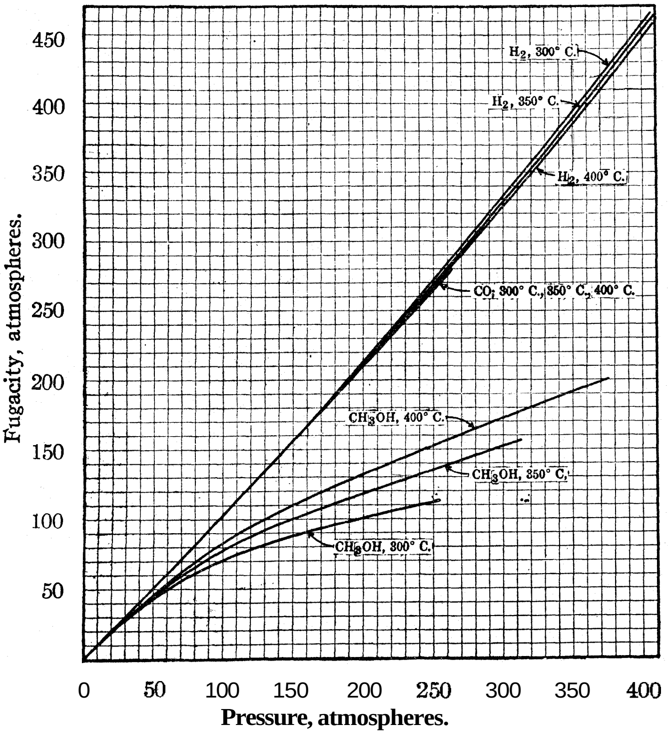


Fig. 2.—Fugacities of H_2, CO and CH_3OH.

It may be of interest to compare briefly our theoretical yields with the yields of methanol which have been obtained in the practical operation of the methanol process. In order to do this it is necessary first to estimate the fugacities of the three gases involved. The results of these calculations are presented in Fig. 2. The data for carbon monoxide were calculated from van der Waals' equation, with $a = 1.487 \times 10^6$ and $b = 39.87$, derived from compressibility data of Amagat[18] which are given up to 400 atm. at 20°. The data for hydrogen were derived, using the rule

---

[18] Amagat, *Ann. chim. phys.*, [6] **29**, 68 (1893).

of Lewis and Randall,[19] from compressibility data of Bartlett, which are given at intervals up to 1000 atm. at 300 and 400°.[20] The data for methanol were calculated from van der Waals' equation, with $a = 9.534 \times 10^6$ and $b = 76.06$, derived from compressibility data of Ramsay and Young[21] which are given up to 78 atm. at 240°. Although the fugacity data are admittedly rough, their use will give better results at high pressures than would the use of the pressures. The fugacities of hydrogen and of carbon monoxide are in general somewhat higher than the pressures

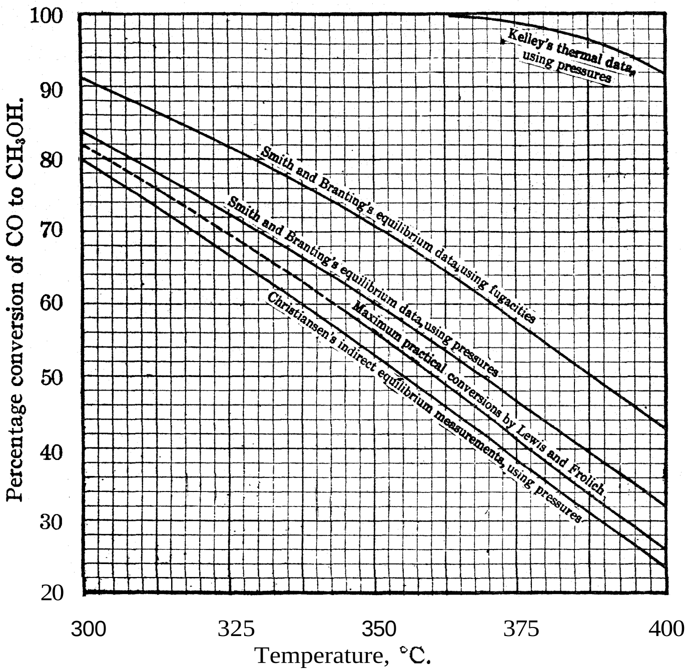


Fig. 3.—Comparison of conversions of CO to CH_3OH as calculated from thermodynamic data and as obtained practically, at several temperatures and at a total pressure of 204 atm. with a gas containing 26% of CO and 70% of H_2.

whereas the fugacities of the methanol are considerably lower than the pressures, as would be expected. This, in each case, results in larger practical yields of methanol than would be predicted from the pressures.

In Fig. 3 are presented comparisons of practical conversions of carbon monoxide to methanol, with the maximum possible conversions predicted

---

[19] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1928, p. 197.

[20] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 5.

[21] *Ibid.*, p. 436.

from various thermodynamic data.[22] The practical yields are taken from Lewis and Frolich. It is seen from the figure that the practical conversions are definitely lower than those predicted from our data, irrespective of any reasonable assumptions as to the fugacities of the gases under these conditions. Lewis and Frolich state that their data at 300° are uncertain. Although it is not possible to draw from these comparisons any definite conclusions regarding the reliability of the thermodynamic data, the comparisons between the predictions from our data and the yields obtained at high pressures are as one would expect. A further comparison may be made between our $K = 2.07 \times 10^{-5}$ and the estimation of $K = 1.1 \times 10^{-5}$ at 400° made by Brown and Galloway[23] from their work on the production of methanol at 180 atm. pressure. It is to be noted in connection with the yields obtained by Lewis and Frolich that, if the gas composition of 26% of carbon monoxide and 70% of hydrogen refers to the original gas, the concentrations of reactants during reaction, especially at the higher temperatures, would be somewhat less because of side reactions. If this were taken into account, the practical yields would be somewhat closer to the theoretical. If the results of the high-pressure work can be relied upon, it would seem that the heat data we have used in the equation giving the temperature function of the free energy are not seriously in error, since the theoretical and experimental curves parallel each other between 300 and 400°.

The value of K we obtained at 304° would seem to have a maximum uncertainty of about 10%; the probable error is not more than about 5%.

Of course, before thermodynamic data can be accurately applied to high pressure work, it would be necessary to know the equations of state for the three gases involved, in mixtures of different compositions. However, the thermodynamic data here presented, together with estimated fugacities, will probably give results which, at present, are sufficient for all practical purposes. A more immediate interest in obtaining accurate thermodynamic data on this reaction at several temperatures would be to show wherein the error lies in the calculations from Kelley's data.

Summary

1. The equilibrium between methanol, carbon monoxide and hydrogen has been experimentally determined at 304° and a total pressure of 1 atmosphere, by a direct method.

2. The equilibrium constant, $K = CH_3OH/(CO)(H_2)^2$, is 5.57×10^{-4} at 303.8°, with a probable error of ± 5%. Calculations from Kelley's

---

[22] The practical conversions used are to be regarded as the maxima obtained in the particular tests referred to. There is no evidence from the curves of conversion against space–velocity, that these conversions are the maximum possible.

[23] Brown and Galloway. Ind. *Eng. Chem.*, **20**, 960 (1928).

low temperature specific heat measurements, extrapolated from room temperature with aid of the best available heat data, give a constant more than 100 times this value. Christiansen's indirect equilibrium measurements give a constant about 34% smaller than our value.

3. The equation for the standard free-energy change in the methanol reaction, derived from our equilibrium measurements and the best available heat data, is $\Delta F = -20{,}857 + 41.17T \log T - 0.01423T^2 - 54.42T$.

4. The yields of methanol at high pressures, as obtained practically and as predicted by our thermodynamic data, compare favorably.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. VIII. THE DETERMINATION OF CHROMIUM IN THE PRESENCE OF MANGANESE, IRON AND VANADIUM

BY H. H. WILLARD AND PHILENA YOUNG

RECEIVED AUGUST 27, 1928 PUBLISHED JANUARY 8, 1929

Introduction

The present volumetric methods for chromium depend upon its oxidation to the hexavalent form by an excess of some suitable reagent and its subsequent reduction, after removal of the excess oxidizing agent, by standard ferrous sulfate added either (1) directly to an end-point which may be determined either electrometrically, with diphenylamine or diphenylbenzidine[1] as internal indicator, or with ferricyanide as external indicator, or (2) in excess, the excess being determined by back titration with standard dichromate or permanganate. In the absence of oxidizing agents such as ferric iron, excess iodide may be used as the reducing agent, the iodine liberated being titrated with thiosulfate. A method using arsenite[2] and another with excess arsenite, followed by back titration with bromate have been described.[3] If persulfate in the presence of silver ions[4] is employed to oxidize the chromium, the excess is destroyed by boiling, and moderate amounts of manganese, converted into permanganate, are reduced to manganous salt by the addition of chloride ions and further boiling. If permanganate is the oxidizing agent, a filtration is always required. In certain cases oxidation is effected by per-

---

[1] The authors have described the use of diphenylbenzidine as an indicator in the titration of chromic plus vanadic acids with ferrous sulfate, Willard and Young, *Ind. Eng. Chem.*, 20,769 (1928). The results using this indicator are the same when chromic acid alone is titrated with ferrous sulfate.

[2] Zintl and Zaimis, Z. *angew. Chem.*, *40*, 1286 (1927); 41, 543 (1928).

[3] Spitalsky, Z. *anorg. Chem.*, *69*, 179 (1910).

[4] Kelley and Conant, J. *Ind. Eng. Chem.*, *8*, 719 (1916).

oxide in alkaline solution.[5] Thus it is seen that all of the methods in use require considerable time to remove the excess of oxidizing agent, and the presence of manganese always lengthens the time for an analysis.

A more rapid volumetric method for chromium, and one in which large amounts of manganese cause no interference or delay, is, therefore, highly desirable. The present paper describes such a method in three different modifications: in one case the chromium is oxidized by a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; in the second method the chromium is oxidized by excess ceric sulfate, nitrite added in slight excess to destroy the ceric salt, then urea to remove all nitrite, after which the chromic acid is titrated with standard ferrous sulfate; in the third method the chromium is oxidized by excess ceric sulfate, sodium azide added in excess to destroy the ceric salt and the chromic acid titrated with standard ferrous sulfate. In all three procedures iron may be present and also vanadium. With the latter element the sum of chromium and vanadium is determined, but it is possible to obtain the percentage of vanadium later with the same solution.

Experimental

In the experimental work chromium was used in the form of a potassium chrome alum solution standardized by the persulfate method, vanadium as vanadyl sulfate and manganese as manganese sulfate. The ceric sulfate solution was that prepared for earlier work[6] and was 0.5 M in sulfuric acid. It was standardized against sodium oxalate.[6] The sodium nitrite,' ferrous sulfate[6] and vanadyl sulfate[8] solutions were standardized against ceric sulfate of known strength.

Preliminary experiments showed that the direct titration of chromic salt in hot solution with ceric sulfate was not possible although the oxidation is more rapid than with any other oxidizing agent. With an excess of ceric salt the oxidation of chromium was very rapid in hot solution. Before this reaction could be studied, a method for removing the excess of ceric salt had to be devised.

A number of reducing agents were tested for their differential possibilities by titrating with them 200 cc. of solution containing 20 cc. of 0.1 *N* ceric sulfate, 100 mg. of chromium as potassium dichromate, 0–40 mg. of

---

[5] The methods mentioned for which references have not been given are described in any of the standard reference texts on Analytical Chemistry or in special texts devoted to Steel Analysis.

[6] Willard and Young, THIS JOURNAL, 50, 1322 (1928); also Furman, *ibid.*, 50, 755 (1928).

[7] Willard and Young, THIS JOURNAL, 50, 1379 (1928).

[8] Furman, THIS JOURNAL, 50, 1675 (1928); Willard and Young, *Ind. Eng. Chem.*, 20, 972 (1928).

vanadium as ammonium vanadate and varying amounts of acid. Using sodium nitrite[7] the reduction of ceric sulfate was selective in the presence of 5–10 cc, of concd. nitric, sulfuric or perchloric acid. The temperature of the solution during titration was held between 50 and 60°. The reaction at the end-point was a little slow but satisfactory and the break in potential averaged 150–200 mv. per 0.05 cc. of 0.1 *N* sodium nitrite. Using sodium oxalate the reduction was selective with 2–5 cc. of concd. sulfuric acid or 5–20 cc. of concd. nitric or perchloric acid per 200 cc. The temperature during titration was 70–80°, the reaction at the end-point about as rapid as with nitrite and the break in potential from 100–150 mv. per 0.05 cc. of 0.1 *N* oxalate. Experiments using either hydrogen peroxide or ferrous sulfate as the reducing agent were not successful.

Oxidation of Chromium with Ceric Salt

A. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Nitrite.—To measured portions of a standard solution of potassium chrome alum were added the indicated volumes of acid and standard ceric sulfate. The volume of the solution at the time of oxidation and the temperature maintained during the oxidation process are shown in Table **I.** After the oxidation the solution was diluted to 200 cc. and the excess ceric sulfate titrated electrometrically at 50–GO° with standard sodium nitrite added from a buret with the tip beneath the surface of the liquid.

TABLE I

OXIDATION WITH EXCESS STANDARD CERIC SULFATE. TITRATION OF EXCESS WITH NITRITE

	Acid, cc.	Vol. at time of oxidation	$Ce(SO_4)_2$, 0.1 N, cc.	Temp for oxidation, °C.	Cr. taken, g.	Cr found. g.
	5	100	40	65 for 5 min.	0.04557	0.04556
	5	100	30	65 for 5 min.	.04557	.04525
HNO_3	5	100	30	65 for 20 min.	.04557	.04556
sp. gr.	5	100	40	65"	.04557	.04554
1.42	5	200	40	65 for 5 min.	.04557	.04561
	10	200	40	65 for 5 min.	.04557	.04561
	5	150	75	65 for 5 min.	.09114	.09108
	10	75	40	65 for 5 min.	.04557	.04355
H_2SO_4,	10	75	40	100[b]	.04557	.04554
sp. gr.	10	75	30	100[b]	.04557	.04487
1.5	10	75	30	100 for 5 min.	.04557	.04562
	20	100	40	100[b]	.04557	.04552
$HClO_4$,	5	100	40	100[b]	.04557	.04562
70%	5	100	40	65"	.04557	.04556

[a] Solution heated to 65° and titrated at once.

[b] Solution heated to 100° and titrated at once.

Forty cc. of ceric sulfate for 45–46 mg. of chromium represents 12 cc. excess of oxidizing agent. The first four experiments show that the rate of oxidation of the chromium increases with the volume of ceric salt used. It is also seen that the oxidation proceeds more quickly in nitric or perchloric acid than in sulfuric acid solution. Variations in acid, volume of solution at time of oxidation and amount of chromium did not alter the accuracy of the method. Other experiments in which as much as 2 g. of iron or 24 mg. of vanadium or both were added were entirely satisfactory. In the presence of iron the reaction with nitrite was somewhat slower, although not more than ten to fifteen minutes was required for a titration and the break in potential was smaller, while in the presence of vanadium the ceric salt used for the oxidation gave accurately the vanadium plus chromium content of the solution. In all later experiments the procedure of oxidizing the chromium with the ceric salt in a volume of 150 cc. by heating to 100° was adopted. If there was no nitric acid present, the solution was allowed to stand for three to five minutes before diluting it to 300 cc. and titrating with nitrite (this dilution gave the correct temperature for the nitrite titration). Such a procedure for chromium is obviously much more rapid than any in use at the present time.

Stability of Nitrite Solution

The supply of 0.1 N sodium nitrite which was used over a period of five weeks remained constant in normality within less than one part in a thousand, even though the stock bottle was opened a number of times during this interval and no precautions were taken to exclude air. Thus nitrite has a decided advantage in this respect over a number of reducing agents.

B. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Oxalate.—Solutions in which the oxidation of the chromium was carried out exactly as indicated in Table I were titrated electrometrically at 70–80° with standard sodium oxalate. These titrations were slightly more rapid than the nitrite reaction provided that iron was absent. Satisfactory results were obtained in the presence of as much as 1 g. of iron but with larger amounts the nitrite titration is to be preferred. Since sodium nitrite solution, however, is more stable than oxalate, it was used in the greater part of the later work.

C. Use of Ceric Sulfate, Removal of the Excess with Nitrite Followed by Urea and Titration of Chromic Acid with Standard Ferrous Sulfate.—Acid solutions of chromic salt similar to those described in Table I were prepared and the chromium oxidized in hot solution with an excess of ceric salt. After cooling to room temperature nitrite was added, from 5 to 15 cc. more than that required to destroy all ceric sulfate, followed at once by urea to remove excess nitrite. After the addition of 25 cc. of sulfuric acid, sp. gr. 1.5, the chromic acid was titrated electrometrically with standard ferrous sulfate. The results for chromium were always low, the error varying from 0.1–1.5 mg. according as 5 to 15 cc. excess of nitrite had been used. It seemed probable, therefore, that quantitative results could be obtained if the volume of nitrite was controlled more accurately. It was found that an excess of 0.25–0.50 cc. gave no trouble and the error with 1.0 cc. was very slight, provided always that any excess of nitrite was removed at once with urea. Results were identical whether the nitrite was added to the solution at room temperature or at 50–60°. In the method finally adopted the chromium was oxidized in hot solution in a volume of 150 cc., the solution diluted to 300 cc., 0.1 *N* sodium nitrite added in rapid drops until the potential indicated that an excess was present, followed at once by 0.2–0.3 g. of urea. After adding sulfuric acid the solution was titrated with standard ferrous sulfate. Results obtained from a number of experiments are given later in Table II.

Effect of the Presence of Manganese. Nitrite Method

Preliminary experiments showed that a manganous salt is oxidized to a considerable extent in acid solution by ceric sulfate with the formation of permanganate, which changes to manganese dioxide if much manganese or nitric acid is present or if the solution is heated. It was also noticed that nitrite is very effective in dissolving manganese dioxide in acid solution. Solutions similar to those used in Table I, containing also varying amounts of manganese, were oxidized in a volume of 150 cc. with ceric salt. During the heating the permanganate color disappeared but a precipitate was not formed unless nitric acid was present, the manganese content high or the chromium content low. It appeared as if some of the manganese was oxidized first by the ceric salt to permanganate, which was effective in oxidizing chromium. The hot solution was diluted to 300 cc. and treated at once with excess nitrite followed by urea, as described in the preceding paragraph. After the addition of sulfuric acid, the chromic acid was titrated electrometrically with 0.1 N ferrous sulfate. Forty cc. of 0.1 N ceric sulfate, an approximately 10 cc. excess, was used for the oxidation. Results are given in Table II.

In experiments in which a precipitate of manganese dioxide was formed, the nitrite had to be added slowly, drop by drop, especially if a nitric acid solution was used or much iron was present, to avoid an excess of nitrite at any time. The end-point was reached directly after the solution had cleared. If no MnO_2 was present the nitrite could be added in much more rapid drops. The total time required for the determination of chromium by either method was seldom more than twenty minutes. Results were most satisfactory in perchloric and in sulfuric acid solutions, and only slightly less satisfactory in the sulfuric acid solutions containing nitric acid. With nitric acid alone quantitative results were obtained but the reduction of the MnO_2 was quite slow. The experiments also show that

TABLE II

OXIDATION WITH CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. REMOVAL OF EXCESS OXIDIZING AGENT WITH NITRITE FOLLOWED BY UREA. TITRATION OF CHROMIC ACID WITH STANDARD FERROUS SULFATE

Acid, cc. (H_2SO_4, sp. gr. 1.5)	Fe, g.	Mn, mg.	V, mg.	$NaNO_3$ excess, 0.1 *N*, cc.	Cr taken, g.	Cr found, g.	Remarks
5	0	25	0	1.0	0.05342	0.05333	Slight MnO_2 ppt.
5	0	25	0	2.0	.05342	.05312	Slight MnO_2 ppt.
5	0	25	0	3.0	.05342	.05303	Slight MnO_2 ppt.
2.5	0	25	0	3.0	.05342	.05304	Heavier MnO_2 ppt.
10	0	10	0	1.0	.05342	.05308	No MnO_2 ppt.
10	0	10	0	0.25	.05342	.05335	No MnO_2 ppt.
10	0	100	0	.25	.05342	.05335	Heavy MnO_2 ppt.
10^a	0	100	0	.25	.10684	.10670	Heavy MnO_2 ppt.
10^b	0	100	0	.25	.02137	.02132	Heavy MnO_2 ppt.
10	2	25	0	1.0	.05342	.05340	No MnO_2 ppt.
5	2	25	0	1.0	.05342	.05338	No MnO_2 ppt.
$5^{c,d}$	2	25	24	1.0	.05342	.05333	No MnO_2 ppt.
HNO_3, (sp. gr. 1.42)							
5	0	20	0	1.0	.05342	.05332	Heavy MnO_2 ppt.
15	0	10	0	1.0	.05342	.05330	Heavy MnO_2 ppt.
5	0	50	0	1.0	.05342	.05338	Heavy MnO_2 ppt.
5	2	25	0	1.0	.05342	.05349	Slight MnO_2 ppt.
$5^{c,d}$	2	25	24	1.0	.05342	.05368	Slight MnO_2 ppt.
$HClO_4$, 70%							
2.5	0	25	0	1.0	.05342	.05341	Slight MnO_2 ppt.
10	0	25	0	0.25	.05342	.05343	Slight MnO_2 ppt.
10	2	25	0	.25	.05342	.05340	No MnO_2 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42); 5 cc. of each acid in the following experiments							
..	0	25	0	0.25	.05342	.05344	Considerable MnO_2 ppt.
..	0	100	0	.25	.05342	.05123	Heavy MnO_2 ppt.
..	0	75	0	1.0	.05342	.05335	Heavy MnO_2 ppt.
..	2	25	0	1.0	.05342	.05335	No MnO_2 ppt.
^{a}	2	25	0	1.0	.10684	.10653	No MnO_2 ppt.
^{b}	2	25	0	1.0	.02137	,02168	Considerable MnO_2 ppt.
^{c,d}	2	25	24	1.0	.05342	,05322	No MnO_2 ppt.

[a] 70 cc. of 0.1 N $Ce(SO_4)_2$ used.

[b] 20 cc. of 0.1 N $Ce(SO_4)_2$ used.

[c] 50 cc. of 0.1 $Ce(SO_4)_2$ used.

[d] Solution cooled to 5–10° before titration with ferrous sulfate.

the reducing action of the nitrite on the chromic acid becomes evident with a large excess of nitrite or with high acid concentration. It is seen that ferric salts are effective in preventing the formation of MnO_2. One extremely important point is that this procedure for chromium is accurate and simple, even in the presence of as much as 100 mg. of manganese.

Since the action between nitrite and MnO_2 is quite rapid in many instances, the possibility of a direct titration with standard nitrite was investigated. Solutions prepared and oxidized as in Table II were **used.** Representative results are shown in Table III.

Table III

Oxidation with Standard Ceric Sulfate in the Presence of Manganese and Iron. Direct Titration with Standard Nitrite

Acid cc. (H_2SO_4, sp. gr., 1.5)	Fe, g.	Mn, mg.	V, mg.	Cr taken g	Cr found, g	Remarks
5	0	10	0	0.05342	0.05347	No MnO_2 ppt.
10	0	75	0	.05342	05364	Considerable MnO_2 ppt.
10	0	100	0	,05342	.05282	Considerable MnO_2 ppt.
10	2	20	0	.05342	.05364	No MnO_2 ppt.
10	1	75	0	.05342	.05367	Heavy MnO_2 ppt.
10"	2	20	24	.05342	.05362	No MnO_2 ppt.
(HNO_3, sp. gr., 1.42)						
5	0	20	0	.05342	.05358	Considerable MnO_2 ppt.
5	0	50	0	.05342	.05347	Heavy MnO_2 ppt.
5	0	75	0	.05342	.05081	Heavy MnO_2 ppt.
5	1	50	0	.05342	?	Too slow
5	1	20	0	.05342	.05359	Considerable MnO_2 ppt.
5[a]	1	20	24	.05342	?	Very slow reaction
($HClO_4$, 70%)						
2.5	0	10	0	.05342	.05359	No MnO_2 ppt.
10	0	25	0	.05342	.05367	Heavy MnO_2 ppt.
10	1	20	0	.05342	.05364	Slight MnO_2 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42), 5 cc. of each acid in the following experiments						
[b]	0	20	0	.10684	.10699	No MnO_2 ppt.
[c]	0	20	0	.02137	,02147	Considerable MnO_2 ppt.
..	2	20	0	.05342	.05367	No MnO_2 ppt.
..	1	50	0	.05342	.05366	Heavy MnO_2 ppt.
[a]	2	20	24	.05342	.05367	No MnO_2 ppt.

[a] 50 *cc.* of 0.1 N $Ce(SO_4)_2$ used.
[b] 70 *cc.* of 0.1 *N* $Ce(SO_4)_2$ used.
[c] 20 *cc.* of 0.1 N $Ce(SO_4)_2$ used.

Sulfuric or sulfuric and nitric acid solutions were most satisfactory, nitric acid solutions least so. Perchloric acid solutions were satisfactory in the absence of iron. With no MnO_2 precipitate the reaction between ceric salt and nitrite was rapid; otherwise, the precaution of adding the nitrite quite slowly to avoid any excess during the titration had to be taken. Even then a titration always required less than ten minutes if a sulfuric or sulfuric and nitric acid solution was used.

Effect of the Presence of Manganese. Oxalate Method

It was found that the direct titration of excess ceric sulfate with oxalate in the presence of MnO_2 precipitate after a chromium oxidation was slightly more rapid than the nitrite titration, In the oxalate method results accurate to a few hundredths of a milligram of chromium were always obtained in solutions containing 5–20 cc. of concd. nitric acid, 5–15 cc. of perchloric acid or 2 cc. of concd. sulfuric plus 5 cc. of concd. nitric acid per 200 cc., the titrations being made at 70–80°. In a sulfuric acid solution the reaction was quantitative but much slower, as was to be expected from earlier work.[6] The results were quantitative with as much as 40 mg. of manganese in the nitric acid solutions, or with 50 mg. of manganese in the perchloric or nitric plus sulfuric acid solutions. When the manganese precipitated out during the oxidation process, the oxalate was added in rather slow drops. The results were satisfactory in the presence of 1 g. of iron, but with more iron the titration became very slow.

Sodium Azide Method

Since hydrazoic acid may be determined by oxidation to nitrogen with excess ceric salt: it seemed important to test the differential possibilities of this reagent for reducing ceric sulfate in the presence of chromic acid. In preliminary experiments 25 cc. of 0.1 N potassium dichromate was diluted with 10 cc. of sulfuric acid (sp. gr., 1.5) and water to a volume of 300 cc. Five to twenty cc. of 0.1 M sodium azide was added and the solution allowed to stand for thirty minutes before titration of the chromic acid with ferrous sulfate. A blank varying from —0.44 to —0.55 cc. was obtained, indicating slight reduction of the chromic acid by the hydrazoic acid. It was thought that some stronger reducing agent in the commercial sodium azide might be causing the trouble, though the blank varied only slightly when the azide content was changed from 5 to 20 cc. One portion of azide solution was purified by acidifying and distilling the hydrazoic acid into sodium hydroxide solution; another portion by acidifying, adding enough dichromate to destroy any stronger reducing agent present and to react with about 10% of the hydrazoic acid and distilling into sodium hydroxide. After adjustment to 0.1 M, 20 cc. portions of these two solutions were tested for their action on dichromate, using the procedure described above. The blank in each case was —0.56 cc. Therefore nothing was accomplished by purifying the azide.

Experiments were then made involving the oxidation of a standard chromic salt solution with excess ceric sulfate, addition of excess azide and titration of the chromic acid electrometrically with standard ferrous sulfate. The oxidation procedure already described was used. After oxidation the solution was diluted to 300 cc., cooled to 35–40°, the amount of azide indicated in Table IV added (a solution of the commercial salt was used) and the solution allowed to stand for the given time. Twenty to 25 cc. of sulfuric acid (sp. gr., 1.5) was added and the chromic acid titrated. In the results given under the column "Cr found" in Table IV,

---

[9] Martin, THIS JOURNAL, 49, 2133 (1927).

a correction of +0.2 mg. of chromium has been added in every experiment, as an absolute error of this magnitude was always evident.

TABLE IV

OXIDATION WITH CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. REMOVAL OF EXCESS OXIDIZING AGENT WITH SODIUM AZIDE. TITRATION OF CHROMIC ACID WITH STANDARD FERROUS SULFATE

Acid cc. (H_2SO_4, sp gr., 1.5)	Fe, g.	Mn, mg.	V, mg.	NaN_3, 0.1 M, cc.	Time azide acted, min.	Cr taken, g.	Cr found, g.	Remarks
5	0	20	0	20	10	0.05369	0.05367	Considerable MnO_2 ppt.
10	0	25	0	20	10	.05369	.05367	No MnO_2 ppt.
20	0	25	0	20	10	.05369	.05364	No MnO_2 ppt.
10	0	25	0	20	5	.05369	.05373	No MnO_2 ppt.
10	0	25	0	30	10	.05369	.05364	No MnO_2 ppt.
10	0	25	0	50	10	.05369	05345	No MnO_2 ppt.
10	0	25	0	20	60	.05369	.05364	No MnO_2 ppt.
10	0	25	0	20	12 hrs.	.05369	.05292	No MnO_2 ppt.
10	0	25	0	30	60	.05369	.05354	No MnO_2 ppt.
10[a]	0	25	0	20	5	.05369	,05364	No MnO_2 ppt.
10[a]	0	25	0	20	10	,05369	.05368	No MnO_2 ppt.
10	0	75	0	20	10	.05369	.05370	Considerable MnO_2 ppt.
10	0	100	0	20	10	.05369	,05348	Heavy MnO_2 ppt.
10	2	25	0	20	10	,05369	.05363	No MnO_2 ppt.
10[b,e]	2	25	24	20	30	.05369	.05360	No MnO_2 ppt.
10[c]	0	25	0	20	10	.10738	.10712	No MnO_2 ppt.
10[d]	0	25	0	20	10	.02147	02152	Considerable MnO_2 ppt.
(HNO_3, sp. gr., 1.42)								
5	0	25	0	20	10	,05369	.05373	Considerable MnO_2 ppt.
15	0	25	0	20	10	.05369	.05365	Heavy MnO_2 ppt.
5	0	50	0	20	10	.05369	.05365	Heavy MnO_2 ppt.
5	2	25	0	20	10	.05369	.05382	Slight MnO_2 ppt.
10[b,e]	2	25	24	20	30	.05369	.05373	Very slight MnO_2 ppt.
($HClO_4$, 70%)								
5	0	25	0	20	10	.05369	.05365	Considerable MnO_2 ppt.
10	0	25	0	20	10	.05369	.05364	Slight MnO_2 ppt.
10	2	25	0	20	10	.05369	,05369	No MnO_3 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42), 5 cc. of each acid in the following experiments								
..	0	50	0	20	10	.05369	.05364	Heavy MnO_2 ppt.
..	0	75	0	20	15	.05369	.05343	Heavy MnO_2 ppt.
..	2	25	0	20	10	.05369	.05365	No MnO_2 ppt.
..	2[b,e]	25	24	20	30	.05369	.05372	No MnO_2 ppt.

[a] NaN_3 added to the solution at 60–65°.

[b] 45 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[c] 70 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[d] 20 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[e] Solution cooled to 5–10° before titration with $FeSO_4$.

The hydrazoic acid acts more slowly on the manganese dioxide than either nitrite or oxalate. Six to eight minutes was always sufficient, however, to dissolve a heavy precipitate. Expts. 10 and 11 indicate that the azide may be added at a higher temperature without causing reduction of the chromic acid. In this warmer solution the effect of the hydrazoic acid may be unpleasant to some persons. If such experiments are conducted in a hood or the solution cooled to 35–40° before the azide is added, the odor of the acid is hardly noticeable. The tendency for the results to be uniformly low by 0.2 mg. of chromium might indicate slight reduction of chromic acid, but the constancy of this error with variation in the amounts of chromium and azide used and in the time the azide acts is difficult to explain. The fact that an error of less than 1 mg. of chromium is caused by leaving the hydrazoic acid in contact with the chromic acid for twelve hours shows that commercial sodium azide is an ideal substance for removing excess of ceric salt after a chromium oxidation. The method is rapid in the presence of large amounts of manganese.

A thermionic voltmeter, Type DP-2, purchased from the General Electric Company was used for the titrations described in this paper The instrument has infinite resistance and can therefore be connected directly to the platinum and silver chloride electrodes throughout a titration without danger of polarization. This makes unnecessary the use of a galvanometer or potentiometer and a continuous reading of the potential is obtained.

Use of Indicator

After the excess of ceric sulfate has been reduced by a very slight excess of nitrite, and the latter destroyed by urea, the chromic acid may be titrated with ferrous sulfate, using about 0.3 cc. of 0.1% diphenylbenzidine or diphenylamine as indicator. Five to 10 cc. of phosphoric acid (85%) must be added and if the solution contains 2 cc. of concd. sulfuric acid in 200 cc. the end-point is sharp and cerous phosphate precipitates so slowly that the solution is hardly opalescent when the titration is finished. If 4 cc. of sulfuric acid is present, the end-point is less distinct but still fairly good. Cerous phosphate does not precipitate at all under these conditions. With more acid the end-point becomes very poor. If too much sulfuric acid is present, a suitable amount of sodium phosphate may be added.

The indicator method has no advantage over the electrometric, because in any case the latter is required to determine the amount of nitrite to be added.

When sodium azide is used to reduce the excess of ceric salt, the color of the indicator is so weakened that a satisfactory titration is impossible.

The application of the methods described above to the rapid determination of chromium in steel will be made the subject of a subsequent paper.

Summary

1. A volumetric method for chromium, more rapid than any in use, has been developed. The chromium is oxidized with excess ceric salt, three possibilities in procedure being described: (u) oxidation with a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; (b) oxidation with excess ceric sulfate, addition of nitrite in slight excess to destroy the ceric sulfate, followed by urea to remove all nitrate, after which the chromic acid is titrated with standard ferrous sulfate; (*c*) oxidation with excess ceric sulfate, the excess being removed with sodium azide, and the chromic acid titrated with standard ferrous sulfate. The excess of nitrite must be small and the time of action short, while with azide a large excess acting for a considerable time has no reducing action on the chromium.

2. Iron does not interfere. If vanadium is present, the sum of the chromium and vanadium is determined.

3. The method is equally applicable and rapid in the presence of large amounts of manganese. Even though some of the latter may precipitate as manganese dioxide during the oxidation, it is readily dissolved by the reducing agent.

4. Diphenylbenzidine or diphenylamine may be used as indicator in method (b) but not in (c).

ANN ARBOR, MICHIGAN

[CONTRIBUTION RROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. IX. PREPARATION AND STABILITY OF SOLUTIONS

BY H. H. WILLARD AND PHILENA YOUNG

RECEIVED AUGUST 27, 1928 PUBLISHED JANUARY 8, 1929

Introduction

The method used by the authors to purify U. S. P. cerous oxalate and to prepare a large supply of ceric sulfate has been described in the first paper in this series.[1] Prom subsequent work,[2] especially from that dealing with the determination of vanadium and of chromium, it seemed important to investigate more thoroughly the grades of ceric oxide available in order to find the most convenient and inexpensive materials for use. Information concerning the stability of ceric sulfate solutions has also been obtained.

---

[1] Willard and Young, THIS JOURNAL, 50, 1322 (1928).

[2] Willard and Young, *ibid.*, 50, 1334, 1368, 1372, 1379 (1928); 51, 139 (1929); *Ind. Eng. Chem.*, 20, 972 (1928).

Experimental

Solutions were prepared from four samples of ceric oxide kindly furnished by Dr. H. S. Miner of the Welsbach Company of Gloucester, New Jersey. The approximate amount of the oxide required for a liter of 0.1 N solution was taken, treated with sufficient sulfuric acid of the density indicated in Table I to make the final solution 0.5 or 1 *M* in sulfuric acid and the paste heated at the proper temperature until the conversion into ceric sulfate appeared complete. This material, when cool, was added to about 500 cc. of water, the liquid heated to 70–80° and filtered. The normality of the solution was determined with standard ferrous sulfate, and from this factor the weight of material required for a liter of 0.1 N solution was calculated as well as the cost of the ceric oxide for a liter of such a solution, based on the price per 500 g. In large quantities the cost would be 20–30% less.

TABLE I

PREPARATION AND COST OF CERIC SULPATE SOLUTIONS

	Material	Sp. gr. of H_2SO_4 used	H_2SO_4 in the $Ce(SO_4)_2$ soln., molar	G. of oxide per liter of 0.1 *N* soln.	Cost of oxide per liter of 0.1 *N* soln. based on price per 500 g.
1	High grade, anhydrous	1.83	0.5	19.2	$0.17
		1.83	1.0	18.9	.17
2	High grade, hydrated	1.5	0.5	22.5	.15
		1.5	1.0	22.3	.15
		1.3	0.5	24.0	.16
3	Commercial, hydrated	1.5	.5	46.9	.05
		1.3	.5	47.3	.05
4	Commercial, anhydrous	1.5	.5	57.9	.10

With Material 1, a temperature of 150–160° was maintained for a half hour to convert the oxide into sulfate. A small amount of the oxide was not attacked. Sample 2 was converted very rapidly by dilute sulfuric acid into ceric sulfate, a temperature of 130–135° being required with acid of sp. gr. 1.5 and 105–110° with acid of sp. gr. 1.3. The ceric sulfate in the former case dissolved in water to give an almost clear solution; in the latter case there was a small amount of unattacked oxide. Sample 3, when treated with acid of sp. gr. 1.5, was heated to 120–125°, and to 110° if treated with acid of sp. gr. 1.3. Sample 4, the commercial anhydrous material, was not satisfactory. The commercial hydrated oxide contained iron and phosphate and a considerable amount of precipitate settled out in solutions prepared from it. The solution decanted from this precipitate was found entirely satisfactory for chromium determinations[2] in which an excess of ceric sulfate was used as the oxidizing agent, the excess being destroyed by sodium azide or by sodium nitrite followed by urea[2] before the titration of the chromic acid with ferrous sulfate. Since the oxide for a liter of such a solution costs only four or five cents, depending upon whether the price per one-half kilo or per fifty kilos of oxide is used, the cost of the reagent for a single chromium determination is very small. There seems to be no reason why this commercial hydrated material cannot be used in all the methods described by the authors[1,2] except in the case of the titration of iodide where the ferric salt might cause trouble. Even when the high grade, hydrated oxide is used, the cost of the reagent is not excessive, being only ten to fifteen cents per liter, depending on the quantity of material purchased.

Stability of Ceric Sulfate Solutions

Furman has given data over a period of twelve weeks on the stability of ceric sulfate solutions containing free sulfuric acid.[3] Table II contains data over a longer period obtained by the authors on four different solutions.

TABLE II

STABILITY OF CERIC SULFATE SOLUTIONS OVER AN EXTENDED PERIOD

Time, weeks	Normality I	II	III	IV
0	0.09493	0.1043	0.05012	0.09410
10	.09488	.1042	.05009	....
16	....	...	,04996	....
20	.09497	...	....	....
27	.09480	...	....	....
33	....	.1044	....	,09400
40	....	.1042	....	....

Solutions I and III were 0.5 M in sulfuric acid, II and IV, 1.0 *M*. Twenty liters each of I and II and 2 liters of III were prepared, and the stock bottles were opened a number of times during the periods indicated. Only with Solution IV is the normality expressed in terms of weight normality. The values for this solution are the most accurate indication of the stability of ceric sulfate, for the portion tested after a 33-week interval had been standing during that time in a sealed flask in a well lighted room. These data indicate that ceric sulfate solutions are far more stable than perrnanganate solutions, the latter oxidizing agent being the only one which is of the same relative oxidizing power as ceric sulfate.

A number of experiments were made to test the stability of ceric sulfate solutions on boiling. In each case 25 cc. of 0.1 N solution was diluted with acid and water to a volume of 100 cc. This solution was boiled gently under a reflux condenser for the stated time, cooled to room temperature and titrated electrometrically with standard ferrous sulfate. The values for the normality after such treatment are given in Table III.

These results show that ceric sulfate solutions containing free sulfuric

---

[3] Furman, THIS JOURNAL, 50, 755 (1928).

TABLE III

STABILITY OF CERIC SULFATE TOWARD HEAT

	Acid per 100 cc., cc.	Time of boiling, hours	Normality of $Ce(SO_4)_2$
H_2SO_4, sp. gr., 1.5	15	0	0.09322
	10	2	.09322
	20	2	.09322
	20	5	.09322
HNO_3, sp. gr., 1.42	10	1	.09111
	5 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09328
	10 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09288
$HClO_4$, 70%	5 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09322
	10 + 10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09310

acid, or sulfuric acid with moderate amounts of nitric or perchloric acid, are extremely stable toward heat. Such solutions, because of their strong oxidizing power, great stability, utility in a hydrochloric acid solution,[1] ease of preparation and small cost, should find extensive use in analytical work.

Summary

1. The types of ceric oxide available for the preparation of ceric sulfate have been investigated. A high grade, hydrated material supplied by the Welsbach Company meets the most exacting requirements, but the commercial, hydrated product is satisfactory in nearly all cases.

2. The cost of such solutions has been shown to be very small, that of the oxide for a liter of 0.1 N solution from the high grade, hydrated material being ten to fifteen cents, and from the commercial, hydrated material four to five cents.

3. The normality of a ceric sulfate solution containing free sulfuric acid has been found to be practically constant over a period of forty weeks. Such a solution is not sensitive to light or air.

4. The normality of a ceric sulfate solution containing free sulfuric acid, or sulfuric acid with a little nitric or perchloric acid, is not changed by boiling the solution for an hour or longer, but the solution loses oxygen if a high concentration of either of the two latter acids is present.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

INVESTIGATION OF SURFACE TENSION CONSTANTS IN AN HOMOLOGOUS SERIES FROM THE POINT OF VIEW OF SURFACE ORIENTATION

BY K. W. HUNTEN AND O. MAASS

RECEIVED SEPTEMBER 10, 1928 PUBLISHED JANUARY 8, 1929

Investigations of surface energy temperature coefficients have shown that for some substances high abnormal values of the Ramsay-Shields constant are obtained. These abnormalities cannot be explained by dissociation. Ramsay and Miss Aston[1] noticed that the constant increases with the number of CH_2 groups in the molecule. Miss Homfray and Guye[2] found for amyl stearate the high value of **3.34,** and similar cases multiplied in number rapidly. Walden and Swinne[3] gave an empirical relation by which they claimed that the Ramsay-Shields constant, K, could be calculated approximately, $K_e = 1.90 + 0.011\ (nA)$, where nA is the sum of the square roots of the atomic weights of the elements in the compound. Each atomic weight is multiplied by the corresponding subscript as given by the formula for the compound.

Just as Ramsay and Shields chose a molecular weight larger than the theoretical in order to account for a low value of their constant, so a high value might be explained by assuming dissociation, for in that case the proper value could be obtained by choosing a molecular weight smaller than the normal. This explanation, which was suggested by Miss Homfray and Guye, is possibly the true one for some cases, but it does not appear reasonable to apply it to a great many others in which dissociation is most unlikely. In this paper, work is described, the incentive of which was to show that high values might possibly be explained in another way. In this proposed explanation it is assumed that there are too many molecules in the molecular surface when the latter is calculated by using the normal molecular volume, but the presence of these extra molecules is ascribed to a cause other than dissociation, namely, orientation. If the axes of the surface molecules are, on the average, perpendicular to the surface, each one effectively occupies a smaller area than it would if it were not so orientated, with the result that a greater number can crowd into a given area.

An homologous series is best suited for an examination of orientation, and for this purpose the fatty acids were chosen, since their orientation in surface films has been so definitely established by the work of Langmuir[4]

---

[1] Ramsay and Aston, *Z. physik. Chem.*, 15,101 (1894).

[2] Homfray and Guye, *J. chim. phys.*, 1,529 (1904).

[3] Walden and Swinne, *Z. physik. Chem.*, *82,290* (1913).

[4] (a) Langmuir, *Met. Chem.* Eng., *15, 468* (1916); (b) THIS JOURNAL, 39, 1848 (1917).

and Adam.[5] Altogether, ten acids were examined and, for comparison, a saturated hydrocarbon, dicetyl. The purification of the compounds used is described, then the method of measuring the surface tensions. The data obtained are tabulated and then discussed from the point of view of the orientation theory.

Purification of Compounds

Propionic Acid.—A specimen of Kahlbaum's acid was purified by crystallization. The procedure consisted in cooling the acid in a flask until crystallization started and then maintaining the temperature of the bath just below the freezing point.[6] The crystals grew slowly and when three-quarters of the liquid had solidified the remainder was rejected. The solid was allowed to warm up until a little melted and this liquid was shaken to wash the crystals and also rejected. The remainder was allowed to melt and was put through the same cycle. This was repeated until a constant melting point was obtained for three successive crystallizations. In all twelve crystallizations were carried out.

The criterion for the melting point was chosen as the condition where a sample two centimeters long in a sealed melting-point tube froze completely within one-tenth of a degree. Great care and patience were exercised in the melting-point determination, as the time required for equilibrium to be established between solid and liquid is long; −22.4" was found to be the melting point after each of the last three crystallizations.

The butyric acid was found to contain acetic acid as an impurity. It was therefore fractionated five times at atmospheric pressure. The fraction boiling between 160 and 163" was converted into the calcium salt by the addition of milk of lime. The solution was evaporated down and the calcium butyrate was filtered out while hot, since, unlike calcium acetate, it is less soluble in hot than in cold water. The salt was crystallized again and butyric acid was liberated by the addition of hydrochloric acid, slightly less than the theoretical quantity calculated on the basis of the calcium butyrate. The mixture was allowed to separate into two layers and the butyric acid removed with a pipet. It was then distilled in a Pyrex apparatus with joints all glass-sealed as far as the receiver. A small amount of aqueous solution came over at a little above 100°. The temperature then rose rapidly to 161.4" and nearly the whole of the acid distilled within 0.9°.

The portion of acid boiling over the 0.9° range was next distilled under reduced pressure in an apparatus which consisted of three bulbs sealed to a mercury pump. One of the bulbs was the tube in which the surface tension was to be measured. The acid, about 25 cc., was frozen in one bulb while the apparatus was evacuated as thoroughly as possible. A small amount (10 to 15 cc.) was then distilled into the third bulb, which was immediately sealed off. The second portion was distilled into the surface tension tube, which in turn was sealed off. The third fraction was used for the determination of the density.

Caproic, caprylic and capric acids were obtained from the Eastman Kodak Company. They were purified in much the same manner as was propionic acid. The whole of the purified substance chosen froze over a range of not more than 0.2 or 0.3°.

Lauric, myristic, palmitic, margaric and stearic acids were Kahlbaum's acids purified by crystallization from 95% alcohol until the melting point was constant. For instance, the stearic acid used was a specimen which was crystallized fifteen times.

---

[5] N. K. Adam, *Proc. Roy. Soc., London*, **99A**, 336 (1921); **101A**, 452, 516 (1922); **103A**, 676,687 (1923).

[6] Maass and Wright. THIS JOURNAL, 43,1098 (1921).

The hydrocarbon dicetyl, or ditriacontane, was obtained through the kindness of Dr. R. F. Ruttan. It was crystallized from alcohol in order to get a solution which could easily be filtered from suspended impurities and then recrystallized several times from ether.

Measurement of Surface Tension.—The surface tensions were measured by the capillary rise method. The temperature bath was a 2-liter beaker of glycerin. Vigorous circulation of the glycerin was maintained by motor-driven stirrers of the propeller type. The temperature was regulated by hand, by means of a gas burner, and it was possible, by means of an auxiliary jet, to keep the temperature constant to within 0.2° over any desired length of time. All of the thermometry involved, except at temperatures below zero, was carried out by means of thermometers for which certificates of calibration of the Reichsanstalt were available. The accuracy is of the order of 0.2° absolute.

Measurements were made on each substance from the melting point up to about 150°. In the case of propionic acid the observations were continued down to the limit of supercooling, and the properties calculated were found to be continuous down to this temperature.

The tube in which the surface tensions were measured was of the type used by Richards,[7] with this modification, that millimeter scales were etched on the two arms of the tube so that the height of a column of liquid could be read directly to 0.1 mm. The capillary was kept vertical by the use of two plumb-lines. The tube was calibrated by making use of Richards' very accurate determination of the surface tension of benzene.

The readings were always taken with a falling meniscus. If necessary the tube was tilted for a moment in order that the liquid might rise, and then fall to its equilibrium position. A reading was not recorded until the top of the column had been stationary for some minutes.

In the case of margaric acid a series of readings was taken both with rising and with falling meniscus, in order to see how much difference there would be. It was found that the two readings differed by as much as 1.7 mm. near the melting point, and did not coincide until the temperature reached 170°; also that those taken with an ascending column did not lie on as smooth a curve as did the others. The descending values give correct results, as a rising column is apt to create an angle of contact due to the viscosity of the liquid. Since margaric acid gave a greater difference between the two values than did any of the others, and since it was the only one of the higher acids examined that contained an odd number of carbon atoms, it was thought of interest to measure its viscosity. The viscosity results are discussed later.

The butyric acid was distilled into the tube as described above. Of the other acids those which are liquid at ordinary temperatures were

---

[7] T. W. Richards and Coombs, THIS JOURNAL, 37, 1656 (1915); 46, 1196 (1924).

poured in through a funnel. In the case of the solid compounds, the tube was put into a steam-jacket and the substance was melted in a specially constructed funnel. In every case the tube was supported at such an angle that the desired amount of melted acid could be introduced without any entering the capillary. The whole apparatus was allowed to cool without being disturbed until the substance had become solid, when the tube could be handled freely. The tube was sealed to a mercury pump and exhausted. It was attached to the pump in the same inclined position as before, in order that, after a preliminary exhaustion, the substance might be melted again by means of a hot water-bath, while under vacuum. After the tube was cool, it was again exhausted and then sealed off. When everything was ready for a series of readings, the substance was entirely melted and then allowed to run into the capillary. These precautions were taken in order to have a fresh surface, as any traces of impurity are likely to collect in the surface after a time and change the surface tension.

Measurement of Density.—The densities, which are required in the calculations, were all measured over the necessary temperature ranges. A dilatometer with a bulb of about 2.5 cc. capacity was used. A millimeter scale was etched on the stem. Known weights of water were weighed with the bulb, and the volume was plotted against scale reading. The volume occupied by any substance under examination could then be read from the curve. Weighings were corrected for air displaced and allowance was made for the expansion (or contraction) of the bulb at temperatures differing from that at which the calibration was carried out. In the case of propionic acid special precautions, as described by Maass and Wright, were taken on account of the volatility of the substance.

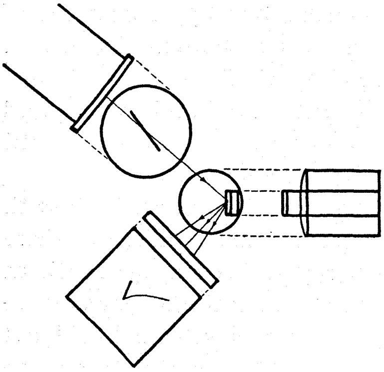


Fig. 1.

Angle of Contact.—It is commonly held that many substances make zero angle of contact with glass, but this cannot be assumed without some verification as the capillary rise method can only be used if such is the case. Specimens of the substances dealt with were examined by the optical method originated by Richards and Carver.[8]

The apparatus is illustrated diagrammatically in Pig. 1. The method consists in directing a slit-shaped beam of light rays upon the junction of solid and liquid surfaces in such a way that the reflected rays may be caught upon a screen. The diagram shows the collimator, the screen

---

[8] Richards and Carver, This Journal, 43,827 (1921).

and the cell containing the liquid. For visual observation a ground-glass plate is used; for more minute examination and for xecording, a photographic plate is substituted for the ground glass. The experiments were carried out in a dark room which itself served as a camera, and the back of an ordinary camera was held in clamps as near as possible to the cell containing the liquid. After the desired image was obtained on the ground glass, the latter was swung aside and the plate-holder was slipped in, exactly as in the regular method of manipulation of a camera. The room was then darkened, the plate was uncovered and the beam of light was turned on for the length of time required for the exposure.

The cell in which the liquid was contained was merely one-half to three-quarter of an inch of test-tube with the bottom flattened. A slip of plate glass about one and one-half inches long stood in the liquid in the cell. The latter was filled over-full, so that the junction between the liquid and the plate glass was not obscured by the wall of the cell. For the same reason it was found best to have both the collimator and the screen tilted toward the cell, so that the actual path of the rays was downward and then up again. This could not be easily shown in the diagram.

It was necessary to have the glass slip absolutely clean. Before it was used, it was cleaned with hot sulfuric acid and bichromate, if necessary, until when it was washed with distilled water and allowed to drain, interference colors would appear in the film of water upon the surface.

In the examination of the higher melting substances (60–70°) it was necessary to use a diminutive electrical heater made by rolling up asbestos paper and nichrome wire with a hollow in the middle in which the cell could be placed. The whole was not more than two inches in diameter, and could be held by a clamp in any position desired. The current was regulated by lamps. One 16-c. p. carbon lamp in series with the heater was suitable in nearly all cases. If the cell was allowed to become too hot the substance would vaporize a little and condense on the upper part of the glass slip which was, of course, comparatively cold, and spoil the photograph.

Richards and Carver placed their cell in a box, the atmosphere in which was kept saturated with the vapor of the substance in question by a dish of the warm liquid. It was not deemed necessary to take this precaution in the present work because the liquids were examined at temperatures but little above the melting point. Even in case of liquids like octane and propionic acid, which were the most volatile ones of which photographs were taken, there was no evidence of evaporation from the edge of the film at ordinary temperatures.

Not only fatty acids but also a few related compounds and a few quite unrelated ones were examined. The degree of difficulty experienced in obtaining the continuous surface may be roughly given as follows: lower fatty acids, water, lower saturated hydrocarbons, higher fatty acids, higher saturated hydrocarbons except paraffin wax, hexadecylene (the only unsaturated hydrocarbon examined), concentrated sulfuric acid, glycerol, paraffin wax.

The end desired was achieved, namely, to show that the surface tension measurements made on the fatty acids were not vitiated by the existence of a finite angle of contact.

Viscosity.—As was mentioned above, it was deemed advisable to measure the viscosity of margaric acid in relation to that of its neighbors in the series. Accordingly the viscosities of palmitic, margaric and stearic acids were measured over a range of temperature.

The viscosities were measured in the same tube as was used for surface tension, which had a 2-cc. bulb just above the capillary. To provide a means of drawing the liquid into the upper bulb, a small tube bearing a cork was plugged into the main tube of the viscosimeter just below the side arm. The narrow tube passed up through a T-tube and was continued to a safe distance away from the vapors of the bath. The T-tube was connected to the top of the viscosimeter by a short length of wide rubber tubing and the top of the T was made air tight by a rubber sleeve through which the small tube could be moved up or down. By applying suction to the side arm of the T, the liquid could be pulled up. Before it passed the upper mark on the way down, the small tube bearing the plug was pulled above the side arm of the viscosimeter in order to allow the air pressure to be the same on both sides. The tube was calibrated at 30.3° with water according to the method described by Maass and Boomer.[9]

The values obtained for the absolute viscosities are given in the following table.

TABLE I

RESULTS OF VISCOSITY DETERMINATIONS

Palmitic acid		Margaric acid		Stearic acid	
Temp., °C.	Viscosity, millipoises	Temp., °C.	Viscosity, millipoises	Temp., °C.	Viscosity, millipoises
74.0	71.7	67.6	92.6	100.7	45.6
91.3	48.0	76.0	74.7	115.9	34.3
111.4	32.8			130.3	26.7
127.5	24.9	107.1	40.3		
144.0	19.4				

When plotted on graph paper it was seen that the viscosity of margaric acid was almost identical with that of stearic acid, both of them being about 10% higher than the viscosity of palmitic acid at 90°.

The results of the determinations of surface tensions and densities are given in Table II, which also contains the surface energies calculated from them.

---

[9] Maass and Boomer, THIS JOURNAL, 44,1709 (1922).

TABLE II

RESULTS OF SURFACE TENSION AND DENSITY DETERMINATIONS

Propionic Acid

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
−36.0			1.05623
−35.1	32.8	558	
−32.6			1.05253
−30.4	32.4	553	
−29.6			1.04918
−25.4	32.0	547	
−21.0			1.03977
−20.4	30.95	535	
−15.4	30.4	527	
−10.8			1.02862
− 8.5	29.7	513	
− 2.9	29.1	506.5	
+ 0.1			1.01713
2.5	28.55	498	
5.0			1.01194
14.9			1.00085
20.9	26.4	432	
23.1			0.99211
29.1			.98560
30.9	25.4	453	
39.4			.97462
40.8	24.5	439.5	
50.5			.96275
53.8	23.2	421	
64.9	22.2	405	
70.8			.94060
80.5			.92988
90.5			.91973
95.4	19.2	359	
98.1			.91157
110.5	17.6	334	
111.4			.89726
118.5			.88948
125.7	15.9	304	
140.3	14.9	289	

Butyric Acid

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
8.6	28.0	565	0.9707
9.7	27.8	562	.9695
18.4	27.1	550	.9615
26.5	26.2	535	.9527
38.9	25.1	517	.9408
50.3	23.8	494	.9292
60.7	22.9	479	.9187
73.2	21.7	459	.9066
77.2	21.4	453	0.9030
68.1	22.3	470	.9119
44.8	24.4	505	.9349
0.1	29.2	590	.9792
1.6	28.7	579	.9773
19.5	26.9	547	.9597
37.5	25.2	520	.9421
91.7	20.1	430	.8838
107.2	18.5	405	
120.7	17.5	382	
131.3	16.4	364	

Caproic Acid

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density. vac.
−20.1			0.9651
−20.0	31.2	760	
−11.2			9574
−10.1	30.7	751.5	
− 0.5			9477
+ 1.6	29.6	730	
6.0	28.9	716	
9.9			.9386
19.9			.9301
25.0			.9254
25.7	27.0	677	.9254
35.6	26.2	660	.9168
49.6	25.1	638	.9045
70.3	23.4	603	.8859
90.7	21.6	565	.8678
100.8	20.7	545	.8591

Caprylic Acid

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density. vac.
16.1	28.5	830.5	0.9157
19.9	28.3	826	.9125
25.3	27.9	818	.9083
29.9	27.7	813	.9044
34.6	27.3	804	.9004
40.1	26.6	785	.8962
45.1	25.9	770	.8921
49.2	25.7	765	
62.4	24.5	734	.8779
79.7	22.8	691	.8639
91.6	22.0	671	.8543
100.2	21.6	662	.8475
115.0	20.3	631	.8354
123.9			.8281
129.1	19.3	603	
142.8	18.3	576	

TABLE II (*Continued*)

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
	Capric Acid		
31.9	27.7	923	0.8931
33.6			.8920
41.7	27.2	910	
50.5	26.9	904	.8789
57.9	26.5	896	.8730
71.2	25.1	857	.8627
90.5	23.4	808	.8480
107.7	22.0	768	.8349
121.4	21.1	742	.8242
140.1	19.7	702	.8096
151.2	19.2	688	
	Lauric Acid		
41.8			0.8740
45.0	28.5	1070	
55.0	27.8	1047	
58.0			.8624
66.0			.8565
67.0	26.8	1018	
76.5			.8485
78.3	26.0	992	
88.5	25.0	961	
91.5			.8370
103.3	23.9	927	
115.5	22.9	893	
122.0			.8152
129.0	21.9	861	
135.5			.8051
141.0	20.8	826	
	Myristic Acid		
76.2	27.0	1120	0.850
66.2	27.6	1135	.856
56.8	28.6	1170	.862
60.3	28.4	1165	.860
74.2	27.3	1125	.851
89.2	25.7	1070	.841
109.2	24.2	1020	.828
129.2	22.7	965	.815
149.3	21.3	915	.801
138.3	22.0	940	.808
119.2	23.6	1005	.822
	Palmitic Acid		
64.3			0.854
65.2	28.6	1280	
69.2	28.2	1270	
74.2			.849
79.2	27.5	1240	
85.2			0.842
89.2	26.7	1210	.839
98.2			.834
99.2	26.0	1180	
109.2	25.3	1160	.827
118.2			.821
119.2	24.5	1130	
129.2	23.8	1100	.813
134.2			.810
139.2	22.9	1060	.807
149.3	22.1	1030	.800
	Margaric Acid		
66.9	27.9	1297	
90.6			0.8355
90.8	26.0	1225	
100.7			.8282
110.9			.8213
112.0	24.4	1164	
126.1	23.8	1128	
129.0			.8092
135.7			.8039
141.0	22.5	1076	
146.5			.7961
	Stearic Acid		
70.0	28.9	1395	0.8480
78.3			.8430
78.5	28.4	1375	
87.5	27.7	1348	
88.0			.8355
95.0	27.1	1326	
98.5			.8292
102.0	26 6	1304	
109.0	26.0	1280	
110.5			.8210
115.5	25.5	1262	
119.0			.8153
121.0	25.1	1245	
130.5	24.4	1217	
131.5			.8066
136.5	23.9	1196	
141.5			.7995
145.0			.7975
150.0	22.9	1157	
	Dicetyl		
73.2	27.2	1890	0.7791
83.7	26.4	1840	.7735

TABLE II (Concluded)

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.	Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
92.2	25.8	1810	0.7680	149.3	21.7	1570	0.7311
101.2	25.1	1760	.7622	123.7	23.4	1670	.7479
110.2	24.4	1721	.7565	86.2	26.0	1820	.7717
129.2	23.0	1640	.7440	119.2	23.7	1680	.7508
139.3	22.4	1610	.7375	139.3	22.3	1600	.7378

The precision which may be claimed in the measurements tabulated above is one part in two hundred for the surface tensions and one part in two thousand for the densities. All values were plotted on large scale graph paper and the temperature coefficients of the surface tensions and the Ramsay-Shields constants were determined from these graphs.

The data of interest are condensed in Table III. The last columns refer to "parachors," the apt name invented by Sugden[10] for the volume temperature relationship suggested by McLeod.[11] The experimental values of the parachor are the average obtained over eighty-degree tem-

TABLE III

CONDENSED DATA

Substance	Total surface energy, ergs	Ramsay-Shields constant	Parachor Obs.	Calcd.	$\left(\frac{\text{Calcd.-obs.}}{\text{Obs.}}\right)100$	Observers[a]
Formic acid	68.3	0.90	93.3	102.2	+9.5	(1)
Acetic acid	58.0	1.35	130.8	141.2	+7.4	(2)
Propionic acid	56.8	1.53	168.7	180.2	+6.8	(3)
Butyric acid	54.6	1.65	209.1	219.2	+4.8	(3)
Caproic acid	53.4	2.04	287.2	297.2	+3.5	(3)
Caprylic acid	53.9	2.12	265.6	375.2	+2.6	(3)
Capric acid	55.2	2.36	447.7	453.2	4-1.2	(3)
Lauric acid	54.4	2.56	532.8	531.2	−0.3	(3)
Myristic acid	54.9	2.80	605.8	609.2	+0.4	(3)
Palmitic acid	54.4	2.92	693.2	687.2	−0.9	(3)
Margaric acid	52.7	3.00	733.2	726.2	−1.0	(3)
Stearic acid	54.6	3.04	778.0	765.2	−1.7	(3)
Ethane	45.7	1.98	110.5	112.2	+1.6	(4)
Propane	50.0	2.15	150.8	151.2	+0.3	(4)
Hexane	45.5	2.11	270.4	268.2	−0.4	(5)
Octane	46.7	2.24	347.2	346.2	−0.3	(6)
Hexacosane	51.0	3.90	1082.0	1048.2	−3.0	(7)
Dodriacontane	52.0	4.20	1322.0	1282.2	−3.1	(3)
Hexacontane	47.0	5.50	248.0	2374.2	−5.1	(7)

[a] (1) Morgan and Neidle, THIS JOURNAL, 35,1856 (1913); (2) Morgan and McAfee, *ibid.*, 33, 1275 (1911); (3) Authors; (4) Maass and Wright, ref. 6; (5) Harkins and Cheng, THIS JOURNAL, 43, 35 (1921); (6) Ramsay and Shields, *Z. physik. Chem.*, 12, 433 (1893); (7) Schenck and Kintzinger, Rec. *trav. chim.*, 42,759 (1923).

---

[10] Sugden, *J. Chem. Soc.*, 125,1177 (1924).

[11] McLeod, Trans. Faraday *Soc.*, **19**, 38 (1923).

perature ranges. For all substances tabulated the parachor varied less than 1% over the eighty-degree range. Sugden discovered the additive character for the parachor and his values for carbon, hydrogen, oxygen and the double bond were used in the calculated values. Data required for the discussion based on experimental determinations not described in this paper are also included in Table III, together with the source from which they were obtained.

The first column in Table III is of particular interest from the point of view of the theory of orientation of Harkins[12] and Langmuir.[4b] Briefly this may be stated as signifying that the surface molecules are orientated with the most strongly attracting groups toward the bulk of the liquid and that the total surface energy is determined by the outer groups. According to this, then, the total surface energy in an homologous series should reach a constant value, and in the case of straight chain compounds the same value for all homologous series should be reached, namely, that of the saturated hydrocarbons. The first of these predictions seems to be proved by the values of the total surface energy of the fatty acids. There is a marked decrease in total surface energy from formic to acetic to propionic acid, but by the time the 4-carbon acid is reached a value *is* obtained which differs only slightly from the values of the subsequent acids up to the 18-carbon acid.

The variation in total surface energy between butyric and stearic acids is given by 54 ± 1 ergs. The question arises whether even this variation really exists. Undoubtedly the experimental determinations of the surface tensions were made with greater accuracy than necessary to detect this variation. However, in spite of the precautions taken in the purification of the compounds some of the rarer acids may have contained sufficient impurity to account for the variations found, and taking into account those acids for which large quantities were available and which could therefore be purified to a greater extent, the variation is given by 54.6 ± 0.3. On the whole, therefore, it may be concluded that the total surface energy reaches a constant value in this homologous series after the first few members of the series. However, as far as can be judged from the total surface energies of the saturated hydrocarbons, the series value for the acids is definitely higher. It is true that dicetyl and hexacosane have values approaching that of the fatty acids and that the low value for hexacontane may easily be due to an impurity in the latter. Nevertheless, taking all the evidence so far established, the value is decidedly less.

It does not seem probable that there is complete orientation in the surfaces of pure liquids such as exists in a monomolecular film spread over the surface of water. That there is a certain amount of orientation

---

[12] Harkins, THIS JOURNAL, 39, 541 (1917).

may explain the rapidity with which the total surface energy reaches a constant value in the fatty acid series. These compounds have a polar group and a tendency for orientation in the surface exists. But this tendency is counteracted by thermal agitation with the result that the surface orientation is partial. By partial orientation is meant that, taken over a time interval, the average position of the axes of the surface molecules is perpendicular to the surface with the polar group nearest the main body of the liquid. The surface orientation differs from regional orientation (which may exist in the bulk of the liquid) both in its greater magnitude and in the fact that it is always in the same direction in the surface, whereas the direction of momentary orientation inside a liquid region changes from instant to instant.

The extent of the orientation in a surface will be increased by a strong polar group and by increased molecular size. In the paraffins, where there is no polar group, it seems probable that there is less chance for orientation and consequently the series constant will be reached far more slowly, which is in agreement with the facts.

The series constants of the fatty acids and the paraffins approach one another. This is, however, no proof of complete orientation since it seems likely that in any case the effect of X on the total surface energy in differentiating $C_nH_{2n+1}X$ from $C_nH_{2n+1}H$ must become nil when n is large enough.

It is desirable to bring more conclusive evidence in support of these views by further experimental determinations of the constants for the saturated hydrocarbon series and work along this line is under way.

The Ramsay–Shields constant K_e increases in a continuous way with length of carbon chain and this might be accounted for by orientation if $K_e = 2.12$ for all equimolecular surfaces. If all the fatty acids are completely orientated, the area occupied by any acid molecule is the same as the area occupied by a formic acid molecule. Hence, the volume which should be considered in the case of the higher fatty acids to obtain equimolecular surfaces is not that given by their molecular volume but by the portion which is proportional to the volume of formic acid. This reasoning gives $K_e = 0.94(M/46)^{2/3}$, where 0.94 is arbitrarily taken as the constant for formic acid (molecular weight 46) and K, the constant for a higher acid of molecular weight M. The values for K, calculated in this way are given in Table IV and are seen to be in reasonable agreement with the experimental values.

The above calculation is anything but rigorous and besides assumes that all the acids are associated to the same extent and have the same density. The agreement between calculated and experimental values may be purely accidental. Another relationship, based on still more dubious reasoning, gave $K_e = N^{4/9}(2.12/3.95)$, where N stands for the

TABLE IV

CALCULATED VALUES FOR THE RAMSAY-SHIELDS CONSTANT, K_e

No. of carbon atoms in acid	K_e, experi*mental*	K_e *calcd.* by $K_e = 0.94$-$(M/46)^{2/3}$	K_e calcd. by $K_e = M^{4/9}$-(2.12/3.95)	No. of carbon atoms *in acid*	K_e, experi*mental*	K_e *calcd.* by $K_e = 0.94$-$(M/46)^{2/3}$	K_e calcd. bv $K_e = N^{4/9}$-(2.12/3.95)
1	0.90	0.94	0.85	10	2.36	2.26	2.36
2	1.35	1.22	1.16	12	2.56	2.50	2.56
3	1.53	1.29	1.38	14	2.80	2.73	2.80
4	1.65	1.45	1.57	16	2.92	2.95	2.92
6	2.04	1.74	1.88	17	3.00	3.06	2.99
8	2.12	2.01	2.14	18	3.04	3.16	3.04

number of carbon atoms in the acid. In Table IV the values of K_e calculated in this way are shown to be in close agreement with all the experimental values and in absolute agreement as far as the last seven acids are concerned. This relationship may, therefore, be used as an empirical one but possessing sufficient accuracy for extrapolating the values of K_e for higher fatty acids.

If the high values of the Ramsay and Shields constant are to be explained by the complete orientation in the surfaces of the fatty acids, then the high values of this constant in the case of the higher paraffins show that these are orientated to the same extent. The fatty acid with **32** carbon atoms would have a value 4.0, which is approximately that found for dicetyl. This might not be so bad were it not for the values of the Ramsay and Shields constant which have been obtained for tristearin and tripalmitin.[13] These are 5.4 and 5.5, respectively, whereas the extrapolated values for straight chain fatty acids of 57 and 51 carbon atoms are 4.9 and 5.1, respectively. In other words, the tristearin molecule has the same effect on the Ramsay-Shields constant as a fatty acid of the same number of carbon atoms, although the latter is three times as long. It seems unlikely, therefore, that the high values for the Ramsay-Shields constant can be accurately interpreted in terms of complete orientation. It is far more striking that hexacontane, tristearin and a fatty acid of similar carbon atom content have practically the same abnormally high value for the Ramsay-Shields constant.

It is of considerable interest to compare simultaneously the Ramsay-Shields constant and the percentage difference of calculated and observed values of Sugden's parachor. The parallelism is perhaps to be expected due to the manner in which the two are related. The figures in Table III show that in both series the Ramsay-Shields constant is first too low and then too high and that the observed parachor is at first too low and then too high. That the latter are too high in the case of the compounds of high molecular weight is established beyond the limit of experimental error.

---

[13] Walden, *Z. physik. Chem.*, **75**, **55** (**1910**).

It has been suggested that where the observed value of the parachor is too low this is due to association, just as the low value of the Ramsay-Shields constant is ascribed to the same cause. If this is so it appears reasonable to suppose that the cause for the abnormally large values of parachor and Ramsay-Shields constant are due to the same cause, whatever it may be. From the nature of the constants the Ramsay-Shields constant is more sensitive to the surface tension factor, while the parachor is more sensitive to the density factor. The former shows a more marked change from the normal than the latter with increase in molecular weight, so that something must be taking place which affects the surface in an abnormal way. That this something is a partial orientation of the surface molecules is a plausible hypothesis. The suggestion that the variation from the normal in the case of the Ramsay-Shields constant is due to the form of the molecule or spiral formation is not sufficient unless orientation in the surface is supposed to take place also.

Summary

The surface tensions and densities of ten fatty acids and one long chain paraffin have been measured over a hundred degree range of temperature and their angles of contact with glass were shown to be zero.

The viscosities of palmitic, margaric and stearic acids were measured.

It was shown that the total surface energies of the fatty acids quickly reach a series constant, whereas the series constant for the paraffins is reached more slowly. As far as can be judged from the known experimental data the two series constants approach each other but do not reach the same value rapidly.

The Ramsay-Shields constant was shown to increase rapidly in the case of the fatty acids and could be represented by the relationship $K_e = N^{4/9}(2.12/3.95)$. The constant was found to have abnormally high values in the case of the higher paraffins.

The parallel variation from the normal of the Ramsay-Shields constant and Sugden's parachor was pointed out and ascribed to the same cause, whatever it might be.

It was shown in the discussion on the total surface energy and the abnormally high values of the Ramsay-Shields constant that the former do not indicate complete orientation at the surface and the latter cannot be calculated quantitatively in terms of complete orientation. Nevertheless, it is suggested that *a* partial orientation takes place in the surface of a pure liquid and that the regularities in the former and the abnormal values of the latter are due to this partial orientation.

MONTREAL, CANADA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE CUDAHY PACKING CO.]

A BACTERIOLOGICAL CONDUCTIVITY CULTURE CELL AND SOME OF ITS APPLICATIONS

BY L. B. PARSONS, E. T. DRAKE AND W. S. STURGES

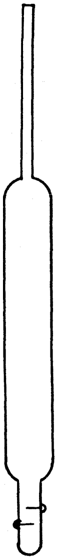
RECEIVED SEPTEMBER 10, 1928 PUBLISHED JANUARY 8, 1929

Introduction

It has been shown in previous investigations[1] that putrefactive anaerobes grown in gelatin or other suitable liquid media cause changes in specific conductance which are proportional to the ammonia production. The latter is an end product resulting from the proteolytic action of these bacteria and hence furnishes a convenient index of biochemical activity and growth.

It appeared that the new method of conductance measurement could be made doubly valuable in studies of the growth of certain anaerobes under various environmental conditions if a conductance cell could be made to function also as a growth vessel. After several trials a type of cell was devised which has been in constant use for a period of two years with satisfactory results.

The method developed has distinct advantages over the usual procedures since a number of consecutive observations may be readily made upon *a* single culture, sealed in glass, thus eliminating all possibility of evaporation, change in anaerobic conditions or chance contamination. The purpose of this paper is to present a description of the cell and to illustrate several applications to definite biochemical problems.



culture cell.

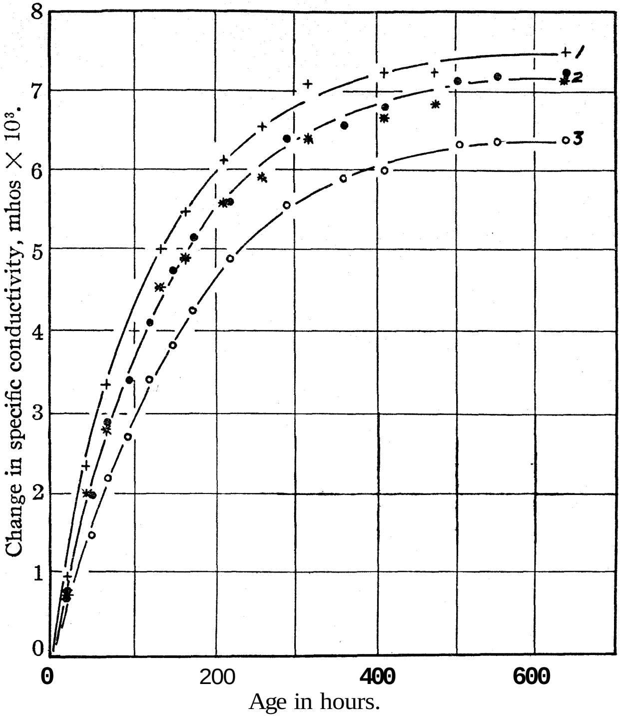
The Conductivity Culture Cell

The cell, Fig. 1, is made of 25-mm. tubing constricted at the lower end to a portion 12 mm. X 40 mm. Electrodes of No. 18 B. and S. gage platinum wire are sealed into the latter so that about 6 mm. of wire projects into the tube. Electrodes are placed 8 to 10 mm. apart. A piece of 8-mm. tubing sealed to the upper portion serves to introduce medium and for inoculation. After inoculation this tube is constricted, evacuated and sealed off. By sealing on 8-mm. tubing, when necessary, the cell can be used indefinitely. The volume of the completed cell is approximately 75 cc. The cell is designed for 5 cc. of culture medium. The large free space is required because most proteolytic organisms evolve considerable quantities of gas. Electrodes must be kept well platinized. Cell constants vary from 1.5 to 2.5. Constants are determined at the end of each run and seldom vary more than 2% from former determinations, showing that repeated sterilization does not affect the cell. It has been found convenient to immerse the cells in 30-mm. tubes containing paraffin oil which are in turn immersed in a water thermostat. The copper lead wires are thus satisfactorily insulated. The latter are arranged to dip into mercury cups making contact with the leads from the bridge.

Parsons and Sturges, *J. Bact.*, 11, 177 (1926); 12, 267 (1926).

Reproducibility of Results

In Fig. 2 curves are plotted showing the change in conductivity with time for C. *putrefaciens* in gelatin at 25°. The data were obtained from two separate runs of five cells each. Run 1 is shown by crosses and Run 2 by circles. Curve 1 represents the maximum rate and Curve 3 the minimum rate observed in the 10 individual cells used. The averages of Runs 1 and 2 show practically perfect agreement and are represented by Curve 2.



O, Minimum, series I and II; ●, average, series I; +, maximum, series I and II; a, average, series II.

Fig. 2.—Reproducibility of results. *C. putrefaciens* in 10% gelatin at 25°.

It has been found that in general the average results obtained with any putrefactive organism using 5 cells per run can be satisfactorily checked in subsequent runs under similar conditions.

Effect of Ph on the Biochemical Activity of C. Sporogenes

The conductivity culture cell is well adapted to the study of the effect of *Ph* on the growth and biochemical activity of anaerobes. In Fig. 3 are presented data on the effect of initial Ph upon the activity of C. *sporogenes*, which is the most common putrefactive organism. The medium was 10% nutrient gelatin adjusted to the required PH by the addition of acid or alkali. PH was measured electrometrically on portions of the sterilized inoculated medium. The cells were incubated at 37.5' and conductances measured at the intervals noted. The sharp maxima at the younger ages are especially noticeable. The tendency of the curves to become more symmetrical at older ages is noteworthy. The zones of optimum reaction at 115 and 211 hours are rather wide. This is due to the high ammonium salt accumulation tending to raise the PH toward the optimum of 8.0 with consequent rapid growth of the organisms. It is evident that the most significant curves are those at 19 and 27 hours.

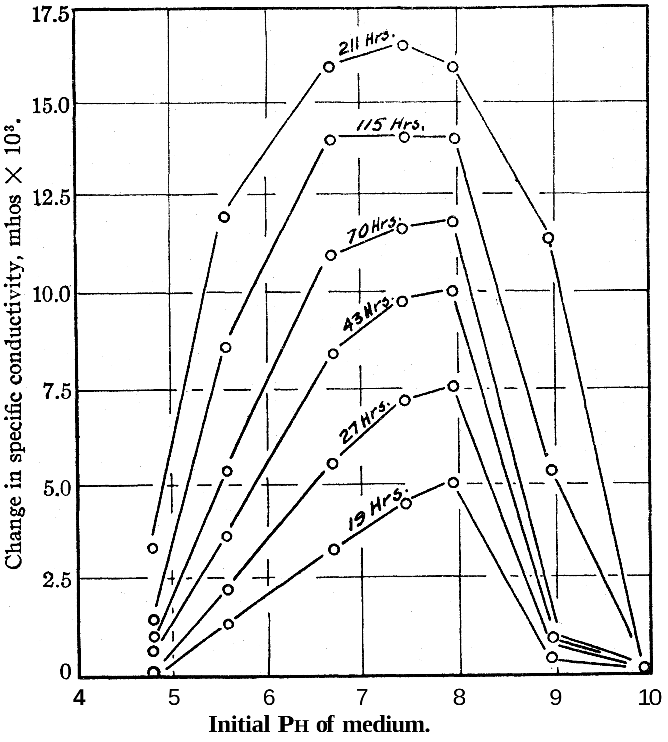


Fig. 3.—Effect of *PH* on biochemical activity of *C. sporogenes* at 37.5° in 10% gelatin.

The Effect of Temperature on the Growth and Activity of C. *Putrefaciens*

The exact effect of temperature on the growth and biochemical activity of proteolytic anaerobes is easily investigated by means of the conductivity culture cell. In Fig. 4 curves are presented showing the averages of runs of 5 cells each at 25, 30, 35 and 40° for *C. putrefaciens* in gelatin medium at PH 7.8.

Since the cells were incubated in separate thermostats and the conductances were measured at the temperatures indicated, it was necessary to refer the data to some standard temperature for comparison. Twenty-five degrees has been selected as the comparison temperature and **all** observations have been calculated to this temperature, using experimentally determined temperature coefficients.

A distinct lag period always occurs in bacterial cultures before growth starts. If allowance is made for this period, the curves in Fig. 4 follow the monomolecular law very closely, that is, the rate of change of conductance is logarithmic. From large scale logarithmic plots the velocity

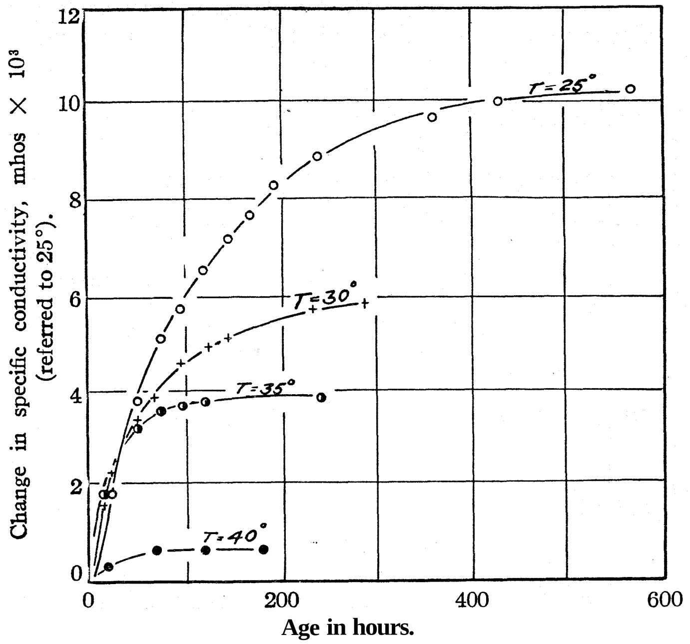
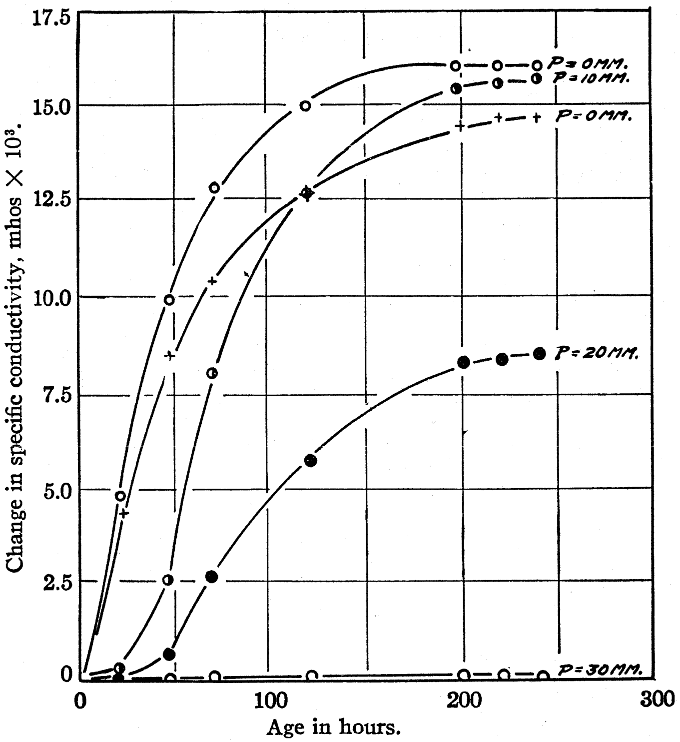


Fig. 4.—Effect of temperature on biochemical activity of C. *putrefaciens* in gelatin.

constants in terms of mhos × 10^3/hours have been calculated to be at 25, 30 and 35°, respectively, 0.0034, 0.0066 and 0.0151. Thus the reaction is more rapid at the higher temperatures, although the quantities of ammonia finally accumulating are much smaller. The velocity is approximately doubled for each 5° increase in temperature, that is, 1.95 for 25–30° and 2.28 from 30–35°.

The Effect **of Oxygen Tension** on the Growth **of** C. *Sporogenes* at **37.5°**

The conductivity culture cell is especially useful in the study of the effect of oxygen tension on the growth of anaerobes. The data presented in Fig. 5 were obtained on C. *sporogenes* by sealing the culture cells at suitable air pressures to give the desired oxygen tensions. It was found that shaking was necessary to secure uniform results at the various oxygen concentrations. Presumably shaking insures saturation of the medium at the tension of oxygen present. A modification of the cell was made by sealing the neck at right angles to the cell. A shaker was arranged in the incubator at 37.5° so that about 15 excursions per minute were made. Since the long axis of the cell was in the horizontal direction a thorough exposure of the medium to the oxygen was obtained. Readings of conductance were made at 30°. This involved exposure of the cells to a lower temperature for about half an hour per day. As a check on the effect of shaking, a cell which was not shaken has always been included in the series. In all cases it has been found that greater increases in conductance occur in the shaken cell.



+, Not shaken; all others shaken 15 r.p.m.

Fig. 5.—The effect of oxygen on *C. sporogenes* in 10% gelatin at 37.5°.

The results are uniform. The lag period becomes more noticeable the higher the oxygen tension, while between 20 and 30 mm. oxygen tension, *C. sporogenes* can no longer grow.

Possible Applications of the Cell

The preliminary results which have been presented show that the cell is peculiarly adapted to the study of such environmental factors as temperature, PH and oxygen tension on the growth and activity of the proteolytic, ammonia-producing anaerobes. There is no reason why the cell might not be successfully applied to the effects of antiseptics, carbon dioxide tension, antagonistic action of salts or the stimulating effect of extractives on this type of organism.

The cell may possibly be applied to the study of any metabolic process involving the production of conducting substances from slightly or non-conducting substrates, for example, the rate of acid production from carbohydrates. It should also lend itself to investigations of the rate of disappearance of conducting substances as, for example, the conversion of nitrate into nitrogen by denitrifying bacteria.

Summary

A new method of studying biochemical activities of certain organisms involving a combined culture conductivity cell has been developed.

This has been successfully applied to the study of biochemical activities of anaerobes at different *P*H's, temperatures and oxygen tensions.

Further possible applications of the new cell have been enumerated.

OMAHA, NEBRASKA

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

THE PREPARATION AND STUDY OF TWO AMMONIUM MOLYBDOTELLURATES

BY V. W. MELOCHE AND WILLARD WOODSTOCK

RECEIVED SEPTEMBER 10, 1928 PUBLISHED JANUARY 8, 1929

Considerable work has been done by Denigès[1] on the adaptation of the complex phosphomolybdate to the colorimetric determination of small amounts of phosphorus. His method depended upon the formation of a blue color upon the addition of stannous chloride to an acid solution of the phosphomolybdate. Since Gibbs[2] and Klein[3] have already mentioned the formation of complex molybdotellurites and tungstotellurites and Pechard[4] has isolated complex molybdoselenites, it was thought that a study of the possible combinations between telluric acid and molybdic acid might furnish the basis for a delicate determination of tellurium similar to the one used for small amounts of phosphorus. The following

---

[1] M. G. Denigb, *Compt. rend.*, 171, 802 (1920).

[2] Gibbs, *Am. Chem. J.*, 17, *177* (1895); *Ber.*, 18, 1089 (1895).

[3] Klein, Bull. *soc. chim.*, *42*, 169 (1884).

[4] *Pechard, Compt. rend.*, 117, 104 (1893).

contribution includes the isolation and analysis of two new molybdotellurates, together with a discussion of some of their properties.

Materials Used

Telluric Acid.—Telluric acid was prepared by the Staudenmeier[5] method. This procedure depends on the chromic acid oxidation of pure tellurium dioxide in dilute nitric acid solution. The product was recrystallized from water solution until it was free from nitric acid, chromic acid and chromic nitrate.

Molybdic Oxide.—Two types of C. P. molybdic oxide were used, the one being 99.9% MoO_3 and the other 85% MoO_3. The latter variety is sometimes referred to as H_2MoO_4 but in this instance it contained variable amounts of ammonia and nitrate. None of the samples contained sodium, potassium or sulfate.

Ammonium Nitrate.—Ordinary C. P. ammonium nitrate was recrystallized from aqueous solution and used without further treatment.

Preparation

The isolation of two different ammonium molybdotellurates was accomplished by the preparation of aqueous solutions containing varying amounts of telluric acid, molybdic acid and ammonium molybdate and subsequent separation of the resulting products by evaporation and crystallization. When an aqueous solution was prepared which contained equimolar portions of telluric acid and molybdic acid and sufficient ammonia to satisfy three of the hydrogens of the H_6TeO_6, clear white crystals separated upon evaporation and cooling which had the formula $3(NH_4)_2O \cdot 2TeO_3 \cdot 6MoO_3 \cdot 10H_2O$. If the above proportion was so changed that the solution contained a considerable excess of molybdic acid in the ratio of one mole of telluric acid to four moles of molybdic acid, and ammonia was present in sufficient quantity to satisfy the telluric acid completely, the solution upon evaporation and cooling would yield clear white crystals having the formula $3(NH_4)_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$. Each of the two different compounds was recrystallized six times and the complete analysis of samples taken from the last crystallization was compared with that of samples taken from the first and second crystallizations. In the instances where the pure molybdic anhydride was used for the preparation, it was found necessary to use aqua ammonia to facilitate the solution of the molybdic oxide. Variations of the general procedure showed that the ammonium ion could also be provided by the addition of ammonium molybdate or ammonium tellurate.

In order to prepare samples for analysis, the crystals were dried by successive washing with alcohol and ether.

Methods of Analysis

Tellurium.—The tellurium content of the compounds was determined by the Lenher-Homberger[6] method in which elementary tellurium was precipitated by the

---

[5] Staudenmeier, *Z. anorg. Chem.*, **10**, 189 (1895).

[6] Lenher and Homberger, THIS JOURNAL, 30, 387 (1908).

combined action of saturated sulfur dioxide water and hydrazine hydrochloride solution upon a dilute hydrochloric acid solution of the sample. It was found desirable to digest the sample in concentrated hydrochloric acid solution before attempting to precipitate the tellurium in the dilute acid solution.

Molybdic Oxide.—The filtrate from the determination of tellurium was evaporated to small bulk on a water-bath and was then fumed with about twenty cubic centimeters of concentrated sulfuric acid. The resulting sample was diluted until the acid concentration was about 6% and the molybdenum was determined by reduction in a Jones reductor and titration with potassium permanganate. The titration was corrected by a blank which was run on the reagents used. Standardization of the permanganate was made upon both sodium oxalate and pure molybdic oxide.

Ammonia.—The original sample was treated with an excess of sodium hydroxide and the liberated ammonium hydroxide distilled into a standard solution of hydrochloric acid. The excess acid was titrated with standard sodium hydroxide and the results were calculated in terms of $(NH_4)_2O$.

Water.—On account of the presence of the ammonium group in the compounds, it was found necessary to modify the ordinary method which is used for the determination of water. Instead of heating the sample and collecting the liberated water in a weighed U-tube which contained concentrated sulfuric acid, the sample was heated in a stream of oxygen in an organic combustion furnace. The porcelain tube contained the usual reduced copper spiral and the finely divided copper oxide. The water evolved was collected in a weighed tube which contained phosphorus pentoxide. Since the oxygen available contained appreciable amounts of hydrogen, it was necessary to pass the oxygen over hot copper oxide and remove the water formed by passing the gas through phosphorus pentoxide before using it in the combustion furnace. The total water obtained in the determination was corrected for that amount due to the oxidation of the hydrogen from the ammonia. This amount of hydrogen was calculated from the results of the ammonia determination already described.

TABLE I

RESULTS OF ANALYSES

For $3(NH_4)_2O{\cdot}2TeO_3{\cdot}6MoO_3{\cdot}10H_2O$	Calcd.	Found	For $3(NH_4)_2O{\cdot}TeO_3{\cdot}6MoO_3{\cdot}7H_2O$	Calcd.	Found
TeO_3	22.62	22.61	TeO_3	13.28	13.20
MoO_3	55.70	55.38	MoO_3	65.36	65.20
$(NH_4)_2O$	10.07	10.18	$(NH_4)_2O$	11.82	12.02
H_2O	11.61	11.75	H_2O	9.54	9.49
	100.00	99.92		100.00	99.91

Properties

Both compounds decompose upon heating at 550° to give a residue containing tellurium dioxide and a small amount of molybdic oxide. This does not constitute a method for the separation of the two oxides since the removal of the molybdic oxide is generally incomplete. If alcohol is added to aqueous solutions of the compounds, finely divided crystals are thrown out of solution. Analysis shows these crystals to have exactly the same composition as those obtained from water solutions by evaporating and cooling. If the dry crystals are allowed to stand over fused calcium chloride in a desiccator, they disintegrate rapidly. The loss of water in the desiccator is not accompanied by the loss of ammonia. The original compounds are readily soluble in water and insoluble in alcohol or ether.

When the ditellurate was recrystallized from a solution containing a large excess of ammonium nitrate, the composition of the compound was unchanged. However, when an excess of ammonium hydroxide was added to the solution and the excess ammonia was driven off by evaporation until a clear solution was obtained, crystals were deposited which upon analysis were shown to have the composition of the monotellurate.

Although it was possible quantitatively to determine the molybdenum in the ammonium molybdotellurates by reduction with stannous chloride,[1] and comparison of the blue color with that obtained from a standard ammonium molybdate solution, it was not found possible to adapt this procedure to the determination of small amounts of tellurium. In the determination of phosphorus the stannous chloride reduces the molybdenum of the ammonium phosphomolybdate, producing the molybdenum blue, while the molybdenum of the excess ammonium molybdate reagent is unaffected. Under similar conditions for tellurium not only is the molybdenum of the molybdotellurate reduced but also the molybdenum of the ammonium molybdate reagent and the tellurium originally present as tellurate.

Summary

Two new ammonium molybdotellurates have been isolated. The analyses of the compounds have been described and formulas assiqned on interpretation of these analyses. The formula for the monotellurate was given as $3(NH_4)_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$, while that of the ditellurate was $3(NH_4)_2O \cdot 2TeO_3 \cdot 6MoO_3 \cdot 10H_2O$.

Some of the general properties of the compounds have been described. It was mentioned that although molybdotellurates were shown to exist, it was not possible to adapt them to the determination of small amounts of tellurium in a procedure similar to that used for the determination of small amounts of phosphorus.

MADISON, WISCONSIN

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 196]

THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT OSMIUM

BY WILLIAM R. CROWELL AND H. DARWIN KIRSCHMAN

RECEIVED SEPTEMBER 14, 1928 PUBLISHED JANUARY 8, 1929

Introduction

In order to facilitate the study of a number of problems concerning the chemistry of osmium, it became desirable to develop a method for the determination of octavalent osmium which would be more rapid and not less reliable than those usually employed. The generally accepted gravimetric methods are those involving the reduction of osmium compounds to the metal; and the most commonly mentioned volumetric method is the iodide method of Klobbie with its modifications. The former methods, while reliable if conducted under proper conditions, are tedious, and require rather elaborate precautions; the latter has a very difficult end-point and, even under the best conditions, it is hard to obtain reproducible results. In the light of the past experience of one of us with ruthenium[1] it was thought that a potentiometric method would prove most satisfactory. It has already been shown[2] that hydrazine compounds reduce octavalent osmium in an alkaline or alcoholic solution to the tetravalent state. It is shown in this paper that this reduction can be carried out in acid solution, and that the progress of the reaction can be followed potentiometrically. Conditions for obtaining reproducible results have been worked out and comparisons made with results obtained by the iodide and gravimetric methods. A study is being made of other reducing agents, such as titanous, chromous and ferrous salts, the results of which will be presented in a later paper.

Apparatus and Materials

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 N potassium chloride-calomel reference half-cell; (3) an oxidation-reduction electrode, made by fusing a platinum wire 2 cm. long and 0.05 cm. in diameter into the end of a small glass tube; (4) a certified buret; (5) a Leeds and Northrup student potentiometer, using a Leeds and Northrup portable galvanometer of 2.84 megohms sensitivity; (6) a 125-cc. beaker as a titration vessel. Calibrated precision pipets were used throughout.

A stock solution of osmium tetroxide in potassium hydroxide was prepared as follows. Metallic osmium, either as purchased or as recovered from residues by reduction with zinc and subsequent ignition in a current of hydrogen, was fused with potassium hydroxide and potassium nitrate. The melt was treated with water and distilled with nitric acid into a solution of potassium hydroxide, whereby a solution of osmium tetroxide was obtained free from ruthenium tetroxide. After acidification the metal

---

[1] Crowell and Yost, THIS JOURNAL, 50, 374 (1928).

[2] (a) Ruff and Borneman, *Z. anorg. Chem.*, 65,436 (1910); (b) *Ber.*, 50,484 (1917); (c) Paal and Amberger, *ibid.*, 40, 1378 (1907).

was again precipitated with zinc from this solution and fused with potassium hydroxide and potassium permanganate. The fused material was again treated with water and distilled from sulfuric acid with a current of oxygen into a definite volume of potassium hydroxide solution of known strength (about 0.4 N), free from traces of organic matter. The solution of osmium tetroxide thus obtained was free from nitric acid, nitric oxide and other volatile impurities. The alkaline solutions of the tetroxide are much more stable than neutral solutions and behave identically on titration.

Hydrazine sulfate solutions were standardized with potassium iodate by the method of Bray and Cuy.[3] The thiosulfate solutions used were frequently compared with a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

Pure hydrobromic acid was obtained by distillation of the 48% acid. The middle fraction was used. All reagents were of standard C. P. quality.

The Potentiometric Method

In order to determine the best conditions for the potentiometric titration of octavalent osmium with hydrazine sulfate, preliminary experiments were conducted at different temperatures using various concentrations of osmium tetroxide and of acid. The acids used were sulfuric, hydrochloric and hydrobromic. Since the last was found to give the most satisfactory end-point, the results with this acid will be described in detail.

In hydrobromic acid solutions below 2 N at room temperatures (20–25°) there is apparently no reaction between hydrazine sulfate and octavalent osmium. As the temperature is raised to 50–60° the occurrence of a reaction is shown by the formation of gas bubbles and by a color change of the solution, which depends upon the acid concentration. At acidities below 1 N an amber color of varying intensity or a black precipitate appears, probably due to hydrolyzed compounds of tetravalent osmium. At acidities above 1 *N* the color change is from light yellow to a deep red.

Under the conditions finally adopted a large drop in potential occurs when four equivalents of hydrazine sulfate have been added for every gram atom of octavalent osmium present. Further additions of the reducing agent produce no additional break, even when five or six equivalents are used. It is evident that the osmium is reduced from the octavalent to the tetravalent state, as is the case in an alkaline or alcoholic solution.[2a] The reaction is probably the following

$$N_2H_6SO_4 + H_2OsO_5 + 6HBr = N_2 + H_2SO_4 + H_2OsBr_6 + 5H_2O$$

Analyses conducted at various temperatures between 60 and 80" gave practically the same results. It is desirable, however, to keep the temperature constant to within 2° because of the rather large temperature coefficient of the cell.

Preliminary experiments showed that quantitative results could not be obtained by a titration of octavalent osmium solutions in open vessels, probably because of a loss of the tetroxide from the acidified solution at the temperature used for the titrations. The procedure finally adopted was as follows. By preliminary direct titration the

---

[3] Bray and Cuy, THIS JOURNAL, 46,858 (1924).

amount of hydrazine sulfate necessary was roughly determined, several per cent. less than the theoretical amount being required because of loss by vaporization. Sealed glass tubes were then prepared containing this amount of hydrazine sulfate, sufficient concentrated hydrobromic acid to make the final acidity 1.5 *N*, and the sample of the stock octavalent osmium solution, these being added in the order mentioned. The tubes were then heated in a boiling water-bath from half an hour to several hours. A tube was then cooled, broken and its contents washed into the titration vessel with from 10–20 cc. of a 1.5 *N* hydrobromic acid solution, the potentiometric titration being completed at 70°. A time of heating longer than half an hour was found to be unnecessary. The same results were obtained even if the quantity of hydrazine sulfate added to the tube before heating was as high as 99% of the total required for titration.

During the electrometric titration the equilibrium voltage is attained within two millivolts in less than three minutes, except in the immediate vicinity of the end-point. The volume of hydrazine sulfate used was determined from the point of inflection in the curve obtained by plotting voltage against volume of reagent added. The voltage drop at the end-point is from 30–60 millivolts for a 0.1-cc. change in volume of reagent added, depending upon the acid concentration and the condition of the platinum electrode. It was found necessary to replace the platinum electrode after 10–12 titrations, since the usual methods of reconditioning electrodes did not prove satisfactory. The inflection is sufficiently abrupt, as is shown by the curve in Fig. 1.

Determinations were made with solutions of osmium tetroxide of various concentrations. Corresponding concentrations of the reducing agent were used. The end-points in the most dilute solutions were not so sharp as in those of higher concentrations but the reproducibility was fairly satisfactory. Amounts of tetroxide as small as 10^{-5} mole may be determined by this method.

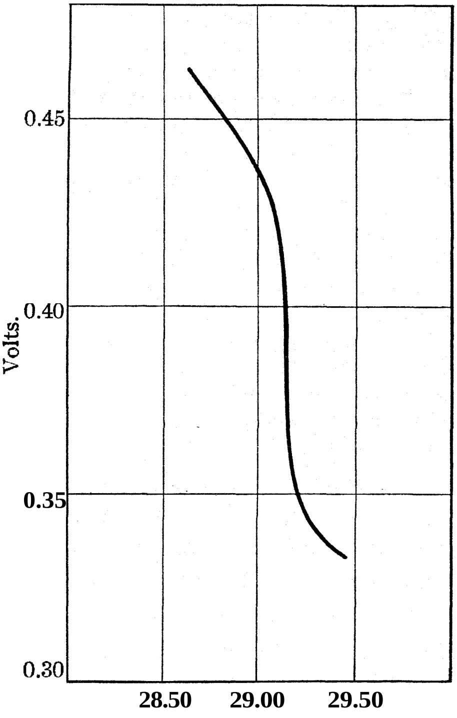


Fig. 1.

The Gravimetric and Iodometric Determinations

Comparative analyses by the gravimetric and iodometric methods were carried out at the same time as those by the potentiometric method, since it was found that the alkaline tetroxide solutions slowly decreased in concentration on standing, owing probably to loss of the osmium tetroxide formed by hydrolysis.

The procedure used in the gravimetric determinations was as follows. A measured portion of the stock osmium solution was pipetted into a glass-stoppered flask, several pieces of zinc sticks (Kahlbaum's) added and the solution made slightly acid with hydrochloric acid. The reaction was allowed to continue for several hours, acid being added from time to time. Too great an acid concentration, especially at the start, causes a too violent evolution of hydrogen and a consequent loss of the osmium tetroxide before reduction to a non-volatile compound has taken place. If the acid concentration is too low, there is a precipitation of basic salts of osmium, from which it is very difficult to reduce the osmium completely. To complete the reduction the solution was digested in the presence of an excess of zinc slightly below the boiling-point until no trace of color was observable. The acidity was then increased to dissolve the zinc completely and rapidly. The osmium metal was then filtered into a weighed Gooch crucible, ignited in a current of pure hydrogen and cooled in a stream of pure carbon dioxide. Duplicate results agreed within 0.2%.

The iodide method as described by Klobbie[4] and Krauss and Wilken[5] was modified as follows: 20 cc. of 2 N hydrochloric acid was heated to boiling, cooled in a current of carbon dioxide and to this was added one gram of potassium iodide dissolved in a few cc. of air-free water. To this solution was added a measured volume (2–10 cc.) of the stock tetroxide solution and the whole allowed to stand for three minutes. The solution was diluted to 200 cc. with air-free water and the liberated iodine titrated with standard thiosulfate solution. Unless these precautions are taken, the results are both high and variable due to the iodine liberated by the action of the oxygen of the air on the iodide. The addition of a few drops of a standard iodine solution enables the disappearance of the blue color of the starch to be determined several times with a given sample. Starch solution was added just before the end-point was reached. Usually from 4 to 6 end-points were determined on each of three samples. A strong light placed beneath the titration vessel aided materially in the determination of the end-point in the deeply colored solution.

The concentration of thiosulfate that seemed most satisfactory was approximately 0.025 *N* and the amounts of osmium solution taken were the equivalent of 8 to 15 cc. of the thiosulfate. The larger sample of tetroxide did not increase the precision of the titration because of the deeper color of the solution. The use of thiosulfate solutions as low in concentration as 0.01 N did not make it possible to obtain results of greater precision since the change in color with addition of thiosulfate was slow. The end-point correction for such solutions is comparatively large.

Under the conditions described the average deviation of each end-point determination from the mean was about 0.25%.

Results of the Potentiometric, Gravimetric and Iodometric Determinations

Table I contains the results of the various determinations by the three methods. For the potentiometric process there was always used 2.005 cc.

---

[4] Klobbie, *Chem. Centr.*, 11, 65 (1898).

[5] Krauss and Wilken, *Z. anorg. Chem.*, 145,151 (1925).

of stock osmium solution, which varied from 0.005 to 0.05 mole per liter. The titration was made at 70° in a total volume of 35-46 cc.

TABLE I

DETERMINATIONS OF OCTAVALENT OSMIUM BY POTENTIOMETRIC, GRAVIMETRIC AND IODOMETRIC METHODS

Normality of acid	Hydrazine solution Millimoles per liter	Hydrazine solution Volume used, cc.	Calcd. concn of osmium soln., millimoles/liter Potentiometric	Calcd. concn of osmium soln., millimoles/liter Gravimetric	Calcd. concn of osmium soln., millimoles/liter Iodometric
1.5	2.880	16.86, 16.88, 16.88, 16.93	24.32	...	24.26
1.5	2.880	16.76, 16.65, 16.73, 16.70	24.00	...	24.02
1.5	4.800	19.98, 20.15, 20.05	...	...	...
2.5	4.800	19.97, 19.98	47.94	....	47.82
1.5	2.880	16.48, 16.50	23.69	23.77	...
1.5	3.840	25.49, 25.43	...	...	...
2.5	3.840	25.41, 25.42	48.73	48.83	48.79
1.5	3.840[a]	12.41, 12.55, 12.57	23.96	...	23.80
1.5	0.960[b]	9.74, 9.76, 9.83	4.683	...	4.728
..	...	... ...	...	22.08	22.12

[a] The concentration of the hydrazine sulfate used to complete the titration was 0.960 millimole per liter.

[b] The concentration of the hydrazine sulfate used to complete the titration was 0.3840 millimole per liter.

From the above table it can be seen that the average difference between the results obtained by the potentiometric titration and those obtained by the gravimetric and iodometric methods is about 0.3%. The agreement of the hydrazine sulfate results among themselves is excellent, the average deviation of each volume required in titration from the mean volume being 0.04 cc.

Summary

A potentiometric method for the determination of octavalent osmium by reduction with hydrazine sulfate solution has been developed and a comparison of the results has been made with those obtained by modifications of the iodometric and gravimetric methods previously described. The accuracy of the method is estimated at 0.2–0.3%.

PASADENA, CALIFORNIA

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

THE HEAT CAPACITY OF METHYL ALCOHOL FROM 16°K. TO 298°K. AND THE CORRESPONDING ENTROPY AND FREE ENERGY

BY KENNETH K. KELLEY[1]

RECEIVED SEPTEMBER 21, 1928 PUBLISHED JANUARY 8, 1929

The measurements of the heat capacities of aliphatic compounds made by Parks and his co-workers[2] have brought forth interesting regularities in the entropies and free energies of members of homologous series. They find that when the members are considered in the liquid state at 298.1°K. there is a definite entropy increase per CH_2 group of about 9 units, while the free energies have the same value within their limits of accuracy. The measurements upon which these conclusions are based do not go below liquid-air temperatures and consequently a very large and uncertain extrapolation is involved in the entropy calculations. It seemed desirable therefore to carry the measurements to liquid hydrogen temperatures in order to throw further light on these regularities. Also, in view of the important theoretical calculations[3] which are being made concerning the formation of aliphatic compounds from carbon monoxide and hydrogen under pressure, accurate values of the entropies of these compounds are now essential.

This paper contains results of measurements on methyl alcohol and will be followed later by data for other substances. Since little extra labor was involved in making the measurements from 90 to 298°K., this region, which Parks covered, was re-investigated and data were obtained for the intervals between his bath temperatures.

Method and Apparatus

The method used has been described by others and the apparatus is of the general type used by them,[4] so that only a brief description seems necessary.

The calorimeter, which is of the design used by Parks, was made from copper tubing and is 6.5 cm. long and 3 cm. in diameter. It is equipped with 38 thin perforated copper disks which are in good thermal contact with the calorimeter walls. These disks are essential for the assurance of rapid heat distribution. A layer of rice paper

---

[1] National Research Fellow in Chemistry.

[2] (a) Parks, THIS JOURNAL, 47, 338 (1925); (b) Parks and Kelley, *ibzd.*, 47, 2089 (1925); (c) Parks and Anderson, *ibid.*, 48, 1506 (1926); (d) Parks and Huffman, *ibid.*, 48,2788 (1926).

[3] (a) Kelley, *Ind. Eng. Chem.*, 18, 78 (1926); (b) Smith, *ibid.*, 19, 801 (1927); (c) Francis, *ibid.*, 20,277 (1928); (d) 20, 283 (1928).

[4] (a) Gibson and Giauque, THIS JOURNAL, 45, 93 (1923); (b) Giauque and Wiebe, *ibid.*, 50,101 (1928).

saturated with Bakelite lacquer was baked on the outside and a bare gold resistance thermometer-heating coil of B. and S. gage No. 40 wire was wound on, the turns being separated by silk thread. The resistance of the coil at 22° is 140 ohms. The gold wire had been annealed previously at temperatures from 350 to 600° for four days. This coil serves both as a heater for the energy input and as a thermometer, as will be described later. Another layer of rice paper and Bakelite lacquer was applied over the coil and the outside covered with gold leaf to decrease radiation. A piece of small-diameter copper tubing one cm. long filled with Wood's metal was soldered to the bottom and serves as a holder for the thermocouple junction. The calorimeter is filled through a small copper tube silver soldered through the bottom. This tube is plugged with solder after filling the calorimeter.

The calorimeter hangs by linen threads inside a heavy metal block, the lower part of which is a copper cylinder of 1.1 kg. mass and the upper part solid lead of about 1.75 kg. mass. This block is equipped with a 260-ohm constantan heater and a thermocouple. All lead wires to external circuits and the calorimeter thermocouple are in good thermal contact with this block, thus minimizing the flow of heat along the wires into the calorimeter.

The block is suspended by heavy twine inside a brass container 21.5 cm. long and 7.5 cm. in diameter. A German silver tube hard soldered in the top of this container serves as support for the container, outlet for the heater lead wires and thermocouples and connection to the evacuating system. On top of this can about 3 kg. of lead is stacked, which together with the heavy block furnishes sufficient heat capacity to make it possible to obtain the entire specific heat curve from 16 to 298°K. without the use of temperature baths other than liquid hydrogen and liquid air. This implies, of course, that measurements be made continuously from about 200" to room temperature; with such a procedure the container warms at just about the right rate.

A pyrex Dewar 76 cm. long and with an inside diameter of 11 cm. was used to contain the temperature baths. This Dewar rests inside a Monel metal can 81 cm. by 16 cm. The top of this can, which is soldered on, is attached to the German silver tube before mentioned and is equipped with an inlet for liquid air or hydrogen, an outlet for the outgoing gas and a safety valve.

The liquid hydrogen is made with a liquefier similar to that described by Giauque and Wiebe and is transferred into the apparatus through a German silver Dewar tube.

Further heat insulation is given by a sheet iron case 100 cm. long and 40 cm. in diameter which is filled with silk floss.

The apparatus is attached by means of a de Khotinsky seal to a glass vacuum line and a pressure of 10^{-5} mm. or better is maintained by a mercury diffusion pump backed by a Nelson oil pump.

The Measurements

The instruments and the method of measuring the energy current and voltage are those described by Gibson and Giauque. The time of energy input was measured with a stop watch which was frequently calibrated against an accurate chronometer of the Department of Astronomy. The temperature rise was measured with the resistance thermometer. The latter was calibrated against the calorimeter thermocouple at intervals of 5 to 15° depending upon the temperature. Care was always taken to have the block and calorimeter within 0.5° of each other when these comparisons were made. Since the resistance was found to increase slightly with the time, it is necessary to make these calibrations for each filling of the calorimeter. The graphical method of Giauque and Wiebe was used in handling these data.

The temperature scale used has been described.[5] The calorimeter thermocouple was compared at 28 points between 14 and 298°K. with one of the laboratory standard couples with conditions as nearly identical as possible with those under which the couple is used. The temperature measurements are considered accurate to 0.05°.

Purification of Methyl Alcohol

The methyl alcohol was Mallinckrodt's "reagent quality." It was allowed to stand over lime for two weeks and carefully fractionated several times. The final product, 300 cc. in volume, had a boiling-point range of 0.01° and density $d_4^{25} = 0.78675$. The value interpolated from the data in "International Critical Tables"[6] is 0.78677, a fortuitous agreement. Also the melting point was very sharp, there being but little pre-melting, which indicates high purity.

Heat Capacities

The heat capacities of methyl alcohol and the mean temperature of each determination are given in Table I and are shown graphically in Fig. 1.

TABLE I

SPECIFIC HEATS OF METHYL ALCOHOL

Temp., °K.	C_p, cal./mole	Temp., °K.	C_p, cal./mole	Temp., °K.	C_p, cal./mole
Crystals				Liquid	
18.80	1.109	97.22	10.23	181.09	16.77
21.55	1.512	111.14	11.23	185.10	16.67
24.43	1.959	114.82	11.48	189.06	16.77
27.25	2 292	117.97	11.64	192.97	16.79
30.72	2.829	118.79	11.64	196.77	16.78
34.33	3.437	121.44	11.75	210.34	16.97
37.64	3.962	125.37	12.18	221.69	17.08
40.87	4.427	129.38	12.28	235.84	17.41
43.93	4.840	133.71	12.64	256.34	17.70
48.07	5.404	147.86	12.97	267.01	18.13
56.03	6.425	152.29	13.69	273.58	18.30
59.53	6.845	153.98	14.12	277.81	18.46
63.29	7.252	157.08	92.5	285.15	18.70
69.95	8.001	157.46	283.4	292.01	19.11
73.95	8.392	159.58	17.92		
77.61	8.735	163.94	11.36		
81.48	9.001	164.14	11.29		
85.52	9.295	166.23	11.63		
89.29	9.693	167.65	11.68		
93.18	9.939				

---

[5] (a) Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, 49, 2367 (1927).

[6] Vol. III, p. 116.

Methyl alcohol has two crystalline forms with the transition at 157.4°K. The transition is not sharp but is of the type first found by Simon[7] for ammonium chloride and later for the other ammonium halides by Simon, Simson and Ruhemann.[8] Such maxima have also been investigated by Giauque and Wiebe[9] in the case of hydrogen bromide and by Millar[10] for manganous oxide. The methyl alcohol transition becomes perceptible at about 145°K. and is over at 160°K.

All attempts to supercool appreciably the high temperature form failed. The experiment which was tried several times consisted in having the block at about 85°K. while the calorimeter was heated *in vacuo* to temperatures well above the transition range and allowed to stand for some time. The vacuum was then broken with hydrogen and the calorimeter and contents cooled rapidly. Even with such temperature differences this form failed to supercool by more than 25° at most.

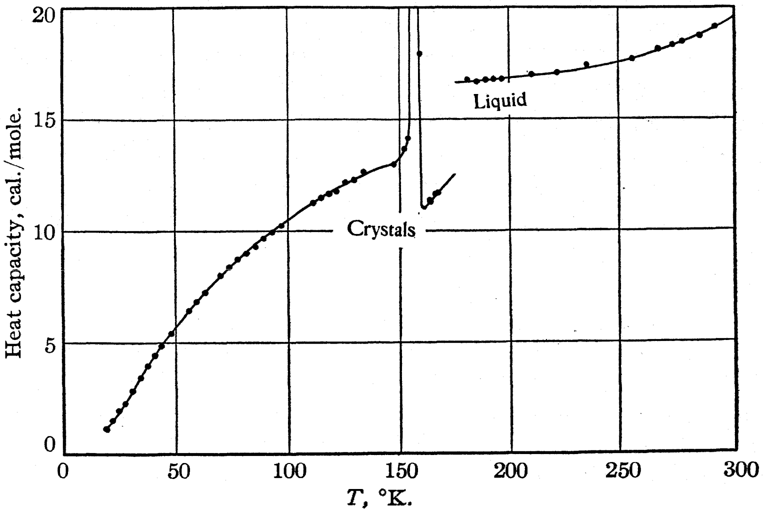


Fig. 1.—Heat capacity in calories per mole of methyl alcohol.

In making the calculations corrections were made for the heat interchange with the block (taking into account the source of error discussed by Giauque and Wiebe),[11] for the heat loss in the calorimeter heater lead wires, for the heat capacity of the small amount of solder used in plugging the calorimeter and for the heat capacity of the empty calorimeter itself. The latter was determined separately in the same manner as when full

---

[7] Simon, Ann. *Physik*, [4] 68,241 (1922).

[8] Simon, Simson and Ruhemann, *Z. physik. Chem.*, 129,339 (1927).

[9] Giauque and Wiebe, THIS JOURNAL, 50,2193 (1928).

[10] Millar, *ibid.*, 50, 1875 (1928).

[11] Ref. 4 b, p. 109.

of methyl alcohol, being filled with hydrogen to increase the speed of heat distribution.

In converting joules to 15° calories the factor 4.185 adopted by "International Critical Tables"[12] was used. All weighings were reduced to a vacuum basis.

The accuracy of the results depends upon the temperature. Below 20° the error may be of the order of 1% due to the rapid decrease of the dR/dT for the resistance thermometer. Between 20 and 40° the error decreases to about 0.2% and remains such to about 130°. Between 130 and 200° the error increases to about 0.5%. Above 200° certain points may be in error by 1% due primarily to large corrections caused by increased radiation. These estimates do not apply to the determinations made in the transition range where the heat capacity is changing very rapidly and where thermal equilibrium is slow. Here the error may be as much as 3%. It is important to note, however, that these determinations are not used in the entropy calculation.

The specific heats are somewhat lower than those obtained by Parks. Above 200° part of this difference (0.5 to 1%) is due to the additional heat interchange correction discussed by Giauque and Wiebe which was made in the present work but not in that of Parks.

The Transition Heat

For the purpose of obtaining the entropy, since specific heat measurements in the transition range could not be made accurately, it was necessary to determine the total heat required to bring one mole of methyl alcohol from a temperature below the transition range to a temperature above it and also to determine what might be called the "mean temperature" of the transition. The latter was determined by the method used by Gibson and Giauque for the melting point of glycerol and also the mean temperature of the hump was read from the C_p vs. T plot. The average of these two values is 157.4°K. Parks reported 161.1°K. for the temperature of transition. The difference between these values is easily explained. Parks measured the temperature during the course of the heat of transition measurements by means of a thermocouple immersed in a central, longitudinal well. This well was soldered to the top of his calorimeter so that it was joined by metal to the calorimeter walls. In the present work with the thermocouple attached to the outside of the calorimeter it was impossible to decide upon any temperature from data taken during a heat of transition measurement since in an ordinary specific heat determination where energy was being supplied slowly a temperature head of from 3 to 5° was built up on the calorimeter walls due to the poor thermal conductivity of the substance in this region. The head was appreciably

---

[12] Vol. I, p. 24.

larger when heat was supplied rapidly, as is done in determining the heat of transition.

The quantity designated "heat of transition" in Table II is the total heat before mentioned from which has been subtracted the area under the "normal" heat capacity curves which were extrapolated to 157.4°K.

TABLE II

HEAT OF TRANSITION, CAL./MOLE

Temp.	1st result	2nd result	Mean
157.4°K.	153.8	154.9	154.3

Melting Point and Heat of Fusion

The melting point and heat of fusion were determined by the methods of Gibson and Giauque. Both values check those of Parks very closely. Table III contains these data.

TABLE III

HEAT OF FUSION, CAL./MOLE

Temp.	1st result	2nd result	3rd result	Mean
157.22°K.	757.2	757.2	756.5	757.0

The Entropy

The entropy, $\int_{16.5}^{298.1} dQ/T$, was calculated in the usual manner. The entropy below 16.5°K. was obtained by extrapolation, using the Debye function with $\Theta = 138$. This procedure in obtaining a value of 0.26 E. U. per mole can certainly cause no appreciable error. The calculations are tabulated below.

TABLE IV

ENTROPY OF METHYL ALCOHOL

0–16.5°K.	extrapolation	0.26
16.5–157.4	crystals	14.18
154.3/157.4	transition	0.98
157.4–175.22	crystals	1.24
757.0/175.22	fusion	4.32
175.22–298.1	liquid	9.28
$S_{298.1}$ for 1 mole of CH_3OH		30.3 ± 0.2 E. U.

This value is 2.3 E. U. lower than that obtained by Parks; however, 1.9 units of this difference is the error in Parks' extrapolation below 90°K. (that is, about 20% of his extrapolated value). This error is due *to* the use of the well-known "*n*" formula of Lewis and Gibson.

The Free Energy

The free energy of formation of methyl alcohol at 298.1°K. may now be calculated from the thermodynamic equation, $AF = \Delta H - TAS$.

The heat of combustion of methyl alcohol was determined by Richards and Davis.[13] Their value when recalculated in terms of the 15° calorie, taking into account the slight error pointed out by Verkade and Coops,[14] corresponds to 170,760 cal. per mole at constant pressure (weighing in vacuum). This result is for the heat of combustion measured at about 291°K. and must be corrected to 298.1°K. by means of the necessary specific heats. This correction is 110 cal. per mole, making the heat of combustion at 298.1° become 170,650 cal. per mole. Combining this latter result with the best values for the heats of formation at 298.1°K. of carbon dioxide and water,[15] one obtains −60,260 cal. for the $\Delta H_{298\cdot1}$ in the above equation.

In calculating $\Delta S_{298\cdot1}$, the entropy of graphitic carbon was taken as 1.3 E. U. per g. atom,[16] that of hydrogen as 29.6 units per mole,[17] and for oxygen 48.9 units per mole.[18] The result is $\Delta S_{298\cdot1} = -54.6$ E. U.

Substituting these values in the equation, the free energy of formation of liquid methyl alcohol is found to be, $\Delta F_{298\cdot1} = -44{,}000$ cal. per mole.

The relation of these results to the thermodynamics of the synthetic methyl alcohol process will be considered elsewhere.

In conclusion the author wishes to thank Mr. G. F. Nelson for the excellent mechanical construction of the apparatus, Professor W. F. Giauque for many helpful suggestions and Professor G. S. Parks of Stanford University for his interest and encouragement.

Summary

1. The specific heat of methyl alcohol has been determined from 16 to 298°K.

2. The transition between the two crystalline forms was found to be of the ammonium chloride type and the heat of transition and temperature were determined.

3. The temperature and heat of fusion were determined.

4. The entropy of methyl alcohol was found to be 30.3 ± 0.2 units per mole.

---

[13] Richards and Davis, THIS JOURNAL, **42, 1599 (1920).**

[14] Verkade and Coops, *Rec. trav. chim.*, **46,903 (1927).**

[15] The heat of formation of water accepted by "International Critical Tables" is **−68,380** cal. at 18°, which would give **−68,320** cal. at 25°. The heat of combustion of β-graphite determined by Roth and Naeser is **−94,270** cal. at about 18° (Z. *Elektrochem.*, **31, 461 (1925)).** The correction for temperature here is negligible due to the fact that CO_2 has the same specific heat as $C + O_2$. This value is considered better than the one selected by "International Critical Tables" previous to the appearance of Roth and Naeser's work.

[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. **464.**

[17] See Ref. 4 b, p. **121.**

[18] Giauque and Johnston, personal communication.

5. The free energy of formation from the elements of liquid methyl alcohol at 298°K. was obtained as —44,000 cal. per mole.

PALO ALTO, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES OF COPPER CATALYSTS PREPARED FROM PRECIPITATED HYDROXIDE.

II. COMPARISON OF SODIUM HYDROXIDE AND AMMONIA AS A PRECIPITATING AGENT

BY PER K. FROLICH, M. R. FENSKE, L. R. PERRY AND N. L. HURD

RECEIVED SEPTEMBER 24, 1928 PUBLISHED JANUARY 8, 1929

In order to obtain copper of the highest purity, the catalysts discussed in the preceding paper were prepared from the hydroxide precipitated from copper nitrate with ammonia. While this method of preparation was useful for a study of the temperature effect, it was apparent that the resulting copper catalysts, on the whole, possessed very low activity.[1] In this respect, as well as in appearance, they resembled the clear, red, very compact metal with low catalytic power which Sabatier[2] prepared by calcination of copper nitrate and subsequent reduction with hydrogen. No doubt both these types of catalysts owe their large particle size and low activity to their high purity, which does not leave any foreign matter to interfere with the crystallization of the metal during reduction.

Reduction of the ammonia precipitated product with hydrogen gave the same low activity that was obtained when using methanol vapor. On the other hand, highly active catalysts were prepared by reduction of the tetra cupric hydroxide precipitated from a boiling copper nitrate solution with sodium hydroxide.[2] This copper, in contrast to that resulting from precipitation with ammonia, was a light violet-colored metal with all the appearance of possessing a smaller particle size.

Experimental Work

These observations pointed to a promoter effect of the small amount of sodium salts which undoubtedly were occluded in the copper hydroxide precipitated with sodium hydroxide. To test this supposition the experiments reported in Table I were made.

Two hundred grams of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in 1500 cc. of water and from this solution the hydroxide was precipitated either with ammonium hydroxide or with sodium hydroxide, as indicated in the table. In each case the hydroxides were heated at 220° in a stream of nitrogen for four hours prior to reduction

---

[1] Frolich, Fenske and Quiggle, THIS JOURNAL, 51, 61 (1929).

[2] Sabatier, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, **1923, p.** 58.

with methanol vapor at the same temperature.' In Expt. 1 copper hydroxide was precipitated with ammonia at 100° and the gel was not further washed, only the supernatant liquor being drawn off. A sample of this same gel was dialyzed for two weeks at about 60° and used in Expt. 2. Expts. 3 and 4 are duplicates of the first two except that sodium hydroxide was used for precipitation instead of ammonia.

TABLE I

RESULTS OF EXPERIMENTS

Experiment	1	2	3	4
Precipitating agent	NH_4OH	NH_4OH[a]	NaOH	NaOH[a]
Wt. of catalyst, g.	0.2297	0.2373	0.2007	0.2917
Temp. of experiment, °C.	385	385	356	356
Life of catalyst, % of time	100	100	23.6	...
CH_3OH decomposed, %	8.0	8.7	44.0	0.0
CH_3OH dec. occur. as CO_2, %	5.3	1.4	4.5	...
CH_3OH dec. occur. as CO, %	5.9	2.1	66.5	...
CH_3OH dec. occur. as $HCOOCH_3$, %	61.2	77.5	17.9	...
CH_3OH dec. occur. as CH_2O, %	27.2	19.2	11.3	...

[a] Dialyzed.

From these data it follows that the catalyst prepared by precipitation with sodium hydroxide without washing possesses a much higher activity than the corresponding catalyst resulting from precipitation with ammonia. This is brought out by the figures for percentage of methanol decomposed, 44.0 and 8.0%, respectively, in spite of the fact that the sodium hydroxide precipitated catalyst is operated about 30° lower than the other. While the ammonia precipitated catalyst is practically unchanged after two weeks' dialysis, the one prepared with sodium hydroxide loses its activity completely at the somewhat lower temperature of 356°. These results point very strongly to promoter action of the sodium salts occluded in the hydroxide.[3]

From Table I it will be seen that the sodium hydroxide precipitated catalyst remained active for only about twenty minutes, at which time the activity proceeded to fall off rapidly until the catalyst became completely dead. The ammonia precipitated catalyst, however, showed constant activity throughout the entire one and one-half-hour period of the run. This temperature effect on the sodium hydroxide precipitated catalyst was studied in a subsequent series of experiments illustrated in Fig. 1. As before, the catalysts were prepared by precipitation with sodium hydroxide with no further washing than drawing off the supernatant liquor on the suction filter. It is seen that by operating at 313°, or below, the activity does not change appreciably with time, but that

---

[3] It will be noticed that the temperature differed for the two types of catalysts. The reason for this was that the activity of the ammonia precipitated catalyst would be too low for reliable measurements at the lower temperature, whereas the sodium hydroxide precipitated copper would lose its activity too rapidly at the higher temperature, as will be apparent from the discussions to follow.

the higher the temperature of operation above this temperature, the shorter is the time the catalyst remains active. At about 380° the catalyst is "dead" before the run can be started. It will also be noted that these curves break very definitely, and for the higher temperatures sharply, indicating the occurrence of some sudden change in the state of the catalyst.

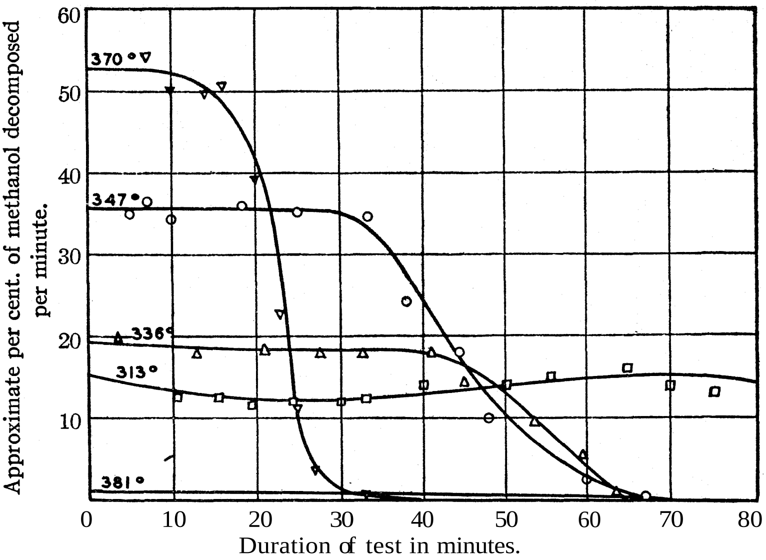


Fig. 1.—Effect of temperature on life of unwashed sodium hydroxide precipitated copper catalysts.

In order to investigate more thoroughly the effect of sodium salts on the catalytic activity of pure copper, a copper hydroxide gel was prepared by precipitation with ammonia and, after careful washing, divided into several portions, to which were added various amounts of sodium nitrate. The following percentages of sodium nitrate, calculated on the basis of copper oxide present, were incorporated in the gel: 0.01, 0.1, 1.0 and 5.0%. From these mixtures catalysts were prepared by the regular procedure of drying and reduction and then run at 300° with the results shown in Table II. The data prove beyond doubt that the sodium nitrate, presumably changed into sodium hydroxide during the preparation of the catalyst, is responsible for the higher activity of the sodium hydroxide precipitated catalyst.

TABLE II

RESULTS OF RUNS

Sodium nitrate added, %	0.0	0.01	0.1	1.0	5.0
Methanol decomposed, %	0.0	0.5	3.6	36.6	**37.0**

Apparently, the dying-out effect observed with the sodium hydroxide precipitated catalysts, as illustrated by Fig. 1, is due to the fusion of the occluded salts, the melting points of sodium nitrate and sodium hydroxide being 316 and 318°, respectively. Since the sodium salt has a marked promoter effect on the copper, it must be in very close proximity to the activated copper atoms or nuclei, and when it melts it apparently covers or blots out these active patches of the catalyst. This explanation is substantiated by the fact that the activity curve breaks only when the temperature is above 313°, as shown by Fig. 1. A pure copper catalyst, such as is prepared by precipitation with ammonia, does not lose its activity within the temperature range studied.

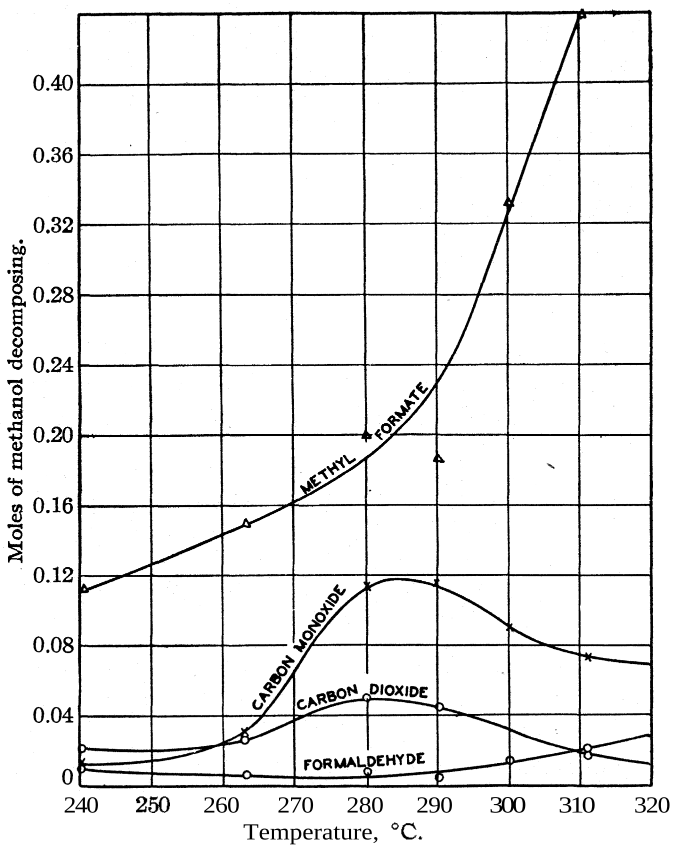


Fig. 2.—Moles of methanol decomposed into the various products as a function of temperature with unwashed sodium hydroxide precipitated copper catalysts. Basis: one mole of entering methanol.

It is to be noted that the decomposition of methanol is an endothermic reaction. Thus when methyl formate is the product, 9000 cal. are absorbed per mole of methanol decomposed, while with carbon monoxide as the product, the corresponding amount of heat is 24,000 cal. Since the reaction is assumed to occur on the surface, it is apparent that the catalyst must be at a somewhat lower temperature than the surrounding space. This may explain why the catalyst is active for a short time even though the temperature is well above the critical value of 315–320°. It also follows that the higher the temperature, the shorter will be the time required for the catalyst to retain this critical temperature, as is brought out by the data in Fig. 1.

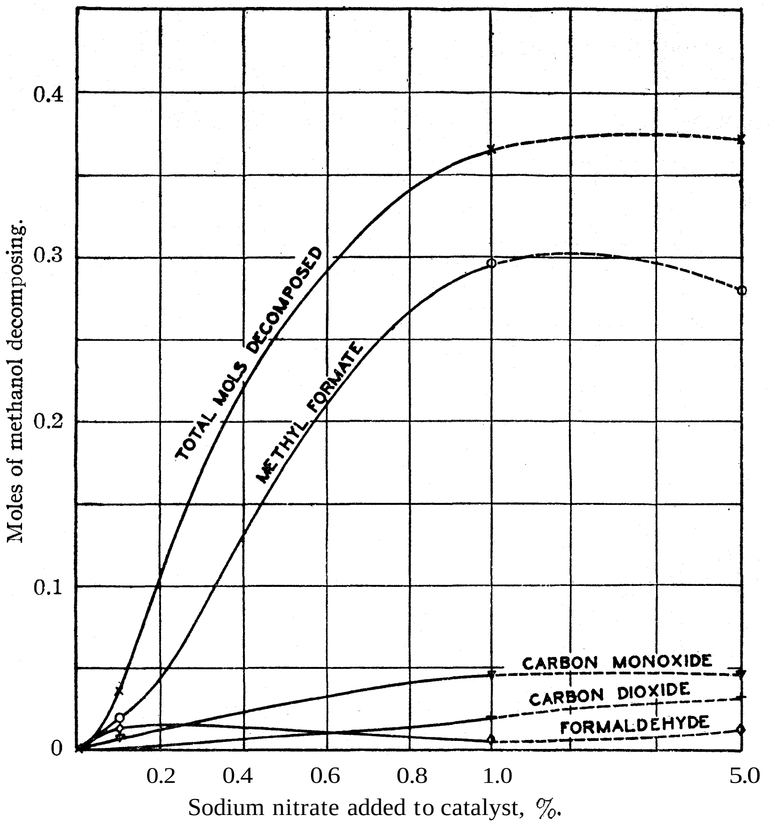


Fig. 3.—Effect of sodium nitrate on the activity of copper and on the mechanism of the decomposition.

In order to incorporate into and promote the copper with other sodium salts of higher melting points, the hydroxide was prepared from copper chloride and copper sulfate by precipitation with sodium hydroxide. The results are shown in Table III, from which it will be seen that the

TABLE III

RESULTS OF EXPERIMENTS

Catalyst	Temp., °C.	Methanol decomposed, %
$CuCl_2$ precip. with NaOH at b. p., unwashed	336–392	0.0
Same but washed with large amt. of water	387400	2.2
$CuSO_4$ precip. with NaOH at b. p., unwashed	385	0.0
Same but washed with large amt. of water	385	0.0
Calcination of copper nitrate	336400	4.0
Calcination of copper acetate	336400	0.0

traces of sulfate and chloride which are retained even on washing are sufficient to poison the catalysts practically completely.

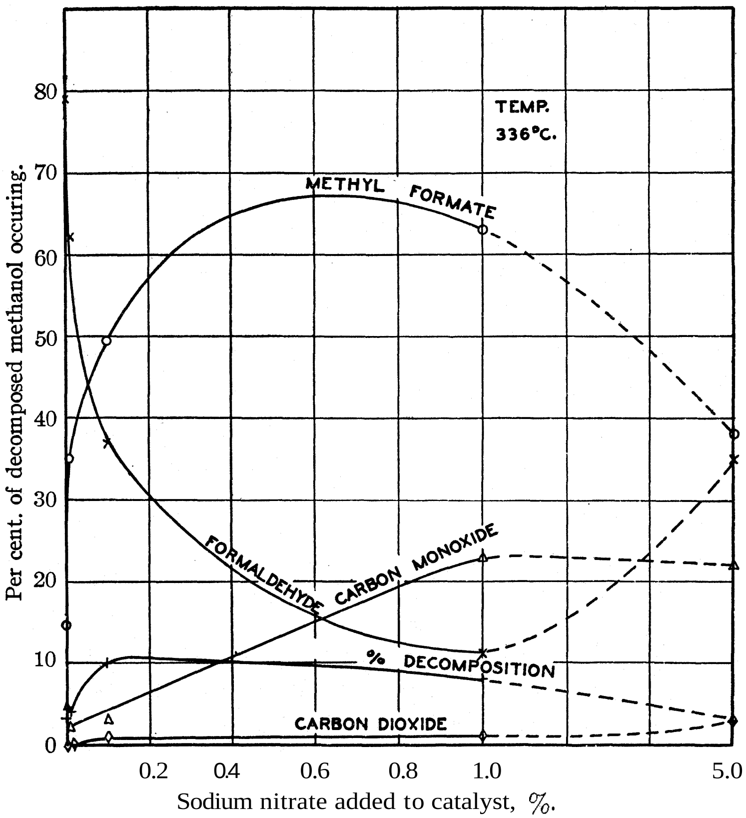


Fig. 4.—Effect of sodium nitrate on the activity of copper and on the mechanism of the decomposition.

Referring again to the sodium hydroxide precipitated catalysts, Fig. 2 shows the effect of temperature on the amounts of the various products of decomposition. The plot shows that the yield of methyl formate increases more rapidly than that of any other constituent, as the temperature increases.

Figs. 3 and 4 give the products of decomposition as a function of the amount of sodium nitrate added to the ammonia precipitated gel. Here it is seen again that the more active catalyst favors the production of methyl formate, as was pointed out in the first paper of this series and in a previous publication on copper catalysts promoted with zinc oxide.[4] Thus, in going from a pure to a promoted copper catalyst, the predominating constituent in the decomposition products changes from formaldehyde to methyl formate.

Conclusions

From the results presented above, it is apparent that copper catalysts prepared by precipitation with sodium hydroxide owe their high activity to the sodium salts thereby incorporated. It is not possible, however, to foretell what effect sodium hydroxide precipitation has on other types of catalysts as, for instance, on those composed of metallic oxides and used in the high pressure synthesis from water gas. In the absence of similar data for such catalysts, it is nevertheless advisable to precipitate with ammonia in order to avoid any disturbing influence of sodium salts, particularly when quantitative information is sought on the effect of promoters purposely added to a catalyst. In the past precipitation with ammonia and with sodium hydroxide has been used interchangeably, and this undoubtedly accounts for the divergent results reported by different experimenters. Thus Patart[5] states that copper gave very poor results when used as a catalyst for the high pressure synthesis of methanol, while Audibert[6] obtained good yields with alkali precipitated copper. Experiments made in the past in this Laboratory with ammonium hydroxide as the precipitating agent check Patart's observations in so far as lack of activity of the pure copper is concerned.[7]

Summary

Copper catalysts prepared by precipitation with sodium hydroxide are more active than those resulting from precipitation with ammonia, the difference being due to promoter action of occluded sodium salts.

These sodium hydroxide precipitated catalysts resemble other promoted copper catalysts in that they favor methyl formate rather than formaldehyde production by decomposition of methanol vapor.

It is suggested that failure to realize the significance of the promoter action of occluded alkali salts may account for the divergent results reported by workers in the field of high pressure synthesis from water gas.

CAMBRIDGE, MASSACHUSETTS

---

[4] Frolich, Fenske and Quiggle, *Ind. Eng. Chem.*, 20, 694 (1928).

[5] Lormand, *Ind. Eng. Chem.*, 17, 430 (1925).

[6] Audibert and Raineau, *ibid.*, 20, 1105 (1928).

[7] Frolich and co-workers, *ibid.*, 20, 1327 (1928).

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

OXIDE CELLS OF CADMIUM, COPPER, TIN AND LEAD[1]

BY CHARLES G. MAIER[2]

RECEIVED OCTOBER 4, 1928 PUBLISHED JANUARY 8, 1929

In the course of a program of investigation of the thermodynamic properties of oxides, the Bureau of Mines at its Berkeley Station carried out a series of measurements upon certain galvanic cells involving oxide electrodes. Work upon zinc oxide previously reported[3] had furnished very satisfactory values of the free energy of formation of the oxide as compared to results by other methods. The results of further measurements were in no case as satisfactory as those upon zinc, for reasons which will appear, and publication was withheld until substantiation by entropy determinations was accomplished. These entropies have now been determined.[4] Enough work was done to indicate the limitations of the cell measurement method for free-energy determination upon oxide materials. Only the briefest outline of methods, and data from the most satisfactory of nearly a hundred cells which were set up in the course of the work, will be recorded here.

Apparatus and Methods

The types of cells used were of three sorts: the ordinary H-type cell with and without a stopcock in the cross arm, unstirred cells with hydrogen electrode and circulating cells with automatic magnetic pump, such as were used by Smith and Woods.[5] The H-cells were used exclusively for measurements in which the oxide electrode was compared to the mercury oxide half-cell in dilute barium hydroxide solution. These cells were completely sealed from the atmosphere, and the contents were stirred to a slight degree by slow rocking upon an oscillating support under the cross arm. Early measurements showed that the transfer of solid oxides between the legs of the H seriously affected the electromotive force when only a glass wool plug was used, so that all measurements recorded here were made in cells with a stopcock, which was opened only during the time of making a voltage measurement. The unstirred cells with hydrogen electrode were similar to the cells with magnetic pump, with the omission of the latter. The cells will not be further described here. When the latter type was used, it is designated below by the symbol $H_2(p)$. All hydrogen cell values recorded have been corrected for barometric pressure and for the effect of water vapor in the saturator, which decreases the partial pressure of hydrogen.

The electrical measuring device was a modern type of potentiometer, with galvanometer sensitive to better than 0.01 millivolt, properly shielded, and whose standard cell was frequently checked against another of a different manufacture. In all cases the

---

[1] Published by the permission of the Director, U. S. Bureau of Mines, Department of Commerce. (Not subject to copyright.)

[2] Metallurgist, Pacific Experiment Station, Berkeley, California.

[3] Maier, Parks and Anderson, THIS JOURNAL, 48,2564 (1926).

[4] Millar, *ibid.*, 51, 207, 215 (1929).

[5] Smith and Woods, *ibid.*, 45, 2632 (1923).

accuracy of the measurement was considerably beyond the limiting deviations of electromotive force involved in the inherent fluctuations of the cell value.

Thermostats were of an automatic oil type, controlled to about 0.03°. The true temperature of the first thermostat nominally at 25° was 24.83°, as determined by a sensitive thermometer with Bureau of Standards calibration, and the second thermostat nominally at 45° had a true temperature of 44.92°

Barium hydroxide solution was used throughout as electrolyte. The material was purified by recrystallization before the solution was made up, was stored in large bottles with atmospheric vent through a long column of soda lime, and was repurified just before use by boiling with shavings of pure zinc in a flask with a trap to prevent re-access of air. Various concentrations were made by aliquot dilution with air-free and carbon dioxide-free distilled water. The solutions were standardized against benzoic acid (Bureau of Standards calorimetric standard).

The sign of the electromotive force given in the tables is such that a spontaneous reaction has a positive e.m.f. and negative free-energy change. In the case of the HgO cells, we have assumed the reaction to be $M + HgO = MO + Hg$, and for the hydrogen cells $M + H_2O = MO + H_2$.

I. Cadmium Oxide

The first cadmium oxide cells were made of a C. P. grade of reddish brown, "amorphous" oxide, which had been further purified of traces of electronegative metals by boiling with C. P. cadmium metal shavings in dilute barium hydroxide solution. The cadmium electrodes were of 8.00 and 12.46% cadmium amalgam, made electrolytically from carefully purified materials. The usual purifications for the preparation of the mercury and mercury oxide for the mercury oxide half-cell were carefully made. The results of the first cells are shown in Table I.

TABLE I

EARLY CADMIUM OXIDE CELLS AT 24.83°

8.00% Cadmium Amalgam

Cell no.	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings averaged	Duration of period of readings, . days	E.m.f.	Av. dev. of mean
A	HgO(red)	0.2426	22	11	+0.8649	±0.0005
B	HgO(red)	.1213	21	11	+ .8551	± .0011
C	HgO(red)	.0809	15	8	+ ,8569	± .0017
D	HgO(yellow)	.2426	22	10	+ .8616	± .0019
				Average	+ .8596	* .0037
1	H_2(p)	.1213	11	7	− .0667	* .0017
2	H_2(p)	.2308	10	8	− .0925	± .0024
3	H_2(p)	.1154	7	4	− .0911	± .0063
4	H_2(p)	.0231	7	6	− .07260	* .0014

The considerable fluctuation of the values for the cells in Table I seemed ascribable to changes in the cadmium oxide. It was noted that the color of the oxide became slightly lighter when the purification was carried out by boiling with cadmium shavings. This phenomenon could be explained by the slow hydration of the oxide. A sample of the oxide was then boiled for about one week in a flask with reflux condenser, using a small amount of barium hydroxide (about **0.0002** M), and protecting from the atmosphere with a barometric mercury trap. At the expiration of this time the color of the oxide had nearly disappeared, indicating that a considerable amount of hydration had occurred. The gradual change with time of electromotive force observed in the first cells may have been due to this action.

Further samples of cadmium oxide were prepared by calcining the purified c. p. "amorphous" oxide and by the ignition of precipitated cadmium oxalate. Material prepared by ignition becomes markedly crystalline, ranging in color from dark brown to blue black, depending on the time and temperature of calcination. A temperature of 750° was found to slow up the hydration without producing too large crystals, which were to be avoided because of the length of time required for the electrolyte to become saturated with oxide. Results for cells with the new materials are given in Table II. Since the presence of the barium hydroxide seemed to increase the rate of hydration, lower concentrations were used.

TABLE II

CADMIUM CELLS AT 24.83°

With Ignited Oxide and 12.46% Amalgam

Cell no.	Oxide form	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings averaged	Time, days	E.m.f.	Av. dev. of mean
E	Oxalate, ign.	HgO	0.0210	8	10	+0.86162	±0.00065
F	Oxalate, ign.	HgO	.0105	4	5	+ .85624	± .00004
G	C. p. ign.	HgO	.0210	4	5	+ .85625	± .0011
H	C. p. ign.	HgO	.0070	8	7	+ .85656	± .0008
"Best" Cells							
I	C. p. ign.	HgO	.0210	7	8	+ .85864	± .00020
I	Duplicate c. p. ign.	HgO	.0210	5	5	+ .85815	± .00006
J	C. p. ign.	HgO	.0105	6	7	+ .85885	± .00040
K	C. p. ign.	HgO	.0070	7	7	+ .85867	± .00053
		Average of "Best" cells			[illegible]	+ .85858	± .00021
5	C. p. ign.	H_2(p)	.0105	5	5	− .07806	± .0025
6	C. p. ign.	H_2(p)	.0210	4	5	− .06810	± .0011
			"Best" H_2 cell			+ .06810	

A preliminary calculation of the free energy of formation of the oxide from the data of Table II showed practically identical results to be obtained with the mercury or hydrogen reference electrode. When Cells I, J and L, which had been at 24.83° for several weeks, were brought to 44.92°, the results shown in the first part of Table III were obtained, but similar calculations did not give results consistent with *new* Cells 7 and **8** compared to the hydrogen electrode.

In order to determine whether this discrepancy was caused by peculiarities of the cadmium amalgam, new Cells Nos. **25** to **28,** inclusive,

TABLE III

FURTHER CADMIUM CELLS WITH IGNITED OXIDES

Description of cell	No. of cell	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
Old Cells	I	HgO	0.0210	14	16	+0.85138	±0.00042
Raised to 44.92°	J	HgO	.0105	5	6	+ .85133	± .00056
	L	HgO	.0052	5	6	+ .85159	± .00043
			Average			+ .85143	± .00010
New Cells:	7	$H_2(p)$	.0070	4	4	.05747	± ,0000
With 12.46%	8	$H_2(p)$	.0035	4	4	− .05880	± .0043
amalgam at 44.92°			Average			− .05813	
New Cells:	25	$H_2(p)$	.2170	7	9	− .01225	± .00050
With electro-	26	$H_2(p)$	.1085	4	4	− .01239	± .00060
deposited Cd	27	$H_2(p)$	.2170	10	13	− .01227	± .00026
44.92° electrodes	28	$H_2(p)$	.0723	9	9	− .01237	± .00017
			Average			− .01232	± .00006
Old Cells brought	I	HgO	.0210	9	12	+ .84670	± ,00034
back to 24.83°	I, dupl.	HgO	.0210	4	4	+ .84721	± .00085
	J	HgO	.0105	9	12	+ .84617	± ,00072
	K	HgO	.0070	7	8	+ .84620	± ,00014
	L	HgO	.0052	9	12	.84668	± ,00016
			Average			+ .84659	± .00033

were set up, using electrodeposited cadmium in place of amalgam. Getman[6] has shown that the electromotive force of electrodeposited metallic cadmium compared to amalgam in cells of the type

$$\text{Cd} \left| \tfrac{1}{2}\text{ Sat. Sol. CdSO}_4 \right| 8\% \text{ Cd Amal.}$$

depends on the history of the cells, and that cells "stabilized" above 40° have an electromotive force of $E = 0.04280 + 0.000170\,(t - 25)$, or 0.04619 volt at 44.92". If this figure be subtracted from —0.01232 volt found for new oxide cells using electrodeposited cadmium, the result, —0.05851 volt, is obtained, a fair check with —0.05813 found from Cells 7 and 8.

In view of the above, old cells which had been at 24.83° for several weeks, and subsequently at 44.92° for several weeks longer, were brought back to 24.83°, with the results shown in the last part of Table III. The satisfactory constancy thus achieved failed to substantiate the original values of these cells.

Some explanation of the behavior of these cells may be found in an accessory experiment. Cadmium amalgam was anodically polarized by a continuous current of 0.5 micro-ampere per square centimeter in barium hydroxide solution for a period of several months. There was produced not cadmium oxide but a hydrated mixture of cadmium and mercury oxides. Although amalgam gives reversible electrodes in neutral or acid solutions, it is certain that such electrodes are not immediately and completely reversible in these basic solutions, where the solubility

---

[6] F. H. Getman, THIS JOURNAL, 39,1806 (1917).

of the mercury oxide is apparently so low that cadmium cannot precipitate mercury ions at these concentrations, or at best can do so only with extreme slowness.

The amalgam cell equivalent to the measurements on Cells 25 to 28, inclusive, may be calculated from Getman's results, as above, and from the free energies of water and mercuric oxide given by Lewis and Randall,[7] to be +0.86235 volt. The data may be summarized as follows

$$\text{New Amalgam Cells} \begin{cases} E_{24.83} = +0.85858 \text{ volt} \\ E_{44.92} = +0.86235 \text{ (equivalent)} \end{cases}$$

$$\text{Old Amalgam Cells} \begin{cases} E_{24.83} = +0.84659 \\ E_{44.92} = +0.85143 \end{cases}$$

A plausible assumption concerning these discrepancies may be that one set represents a cell reaction forming hydroxide and the other oxide. Getman's results for a-cadmium, the supposed stable form, are represented by the equation E = 0.04742 – 0.000200 $(t - 25)$, from which, for the reaction Cd, + Hg = Cd amalgam, $\Delta F_{298} = -2188$ cal., and $\Delta H_{298} = -4940$ cal. (from the differential Gibbs-Helmholtz equation). From the summarized measurements above, we have for the reaction Cd amalgam + HgO = CdO + Hg, or, alternatively, Cd amalgam + HgO + H_2O = $Cd(OH)_2$ + Hg

$$\text{New Cells} \Big\{ \qquad\qquad \text{Old Cells} \begin{cases} \Delta F_{298} = -39{,}068 \\ \Delta H_{298} = -35{,}756 \end{cases}$$

Combining the results of Getman's work with these values, and taking the free energies of mercury oxide and liquid water as –13,808 and –56,560, respectively, from Lewis and Randall, if the new cells represent oxide formation, $\Delta F^{\circ}_{298}(\text{CdO}) = -55{,}618$; $\Delta H_{298} = -63{,}584$. From these figures, A S for the formation of CdO from its elements is –26.73. Lewis and Randall give for the entropy of solid cadmium, $S_{298} = 11.80$; but instead of their value for oxygen, $S_{298}(^1/_2O_2) = 24.0$, we shall use 24.47, based on recent unpublished determinations of the entropy of oxygen at the boiling point and 1 atmosphere (40.57), and the data of Scheel and Heuse[8] (8.37) from thence to room temperature. From these quantities, $S_{298}(\text{CdO}) = 9.54$.

From the data of the old cells, similar calculations lead to the result for the formation of cadmium oxide: $\Delta F^{\circ}_{298} = -55{,}064$; $\Delta H_{298} = -62{,}305$; $S_{298} = 11.98$. The data of Millar[9] lead to a value for cadmium oxide, $S_{298} = 13.17$, indicating that the old cells more nearly represent the cell reaction involving CdO. Recalculating the results for the new cells on the basis of cell reaction to form $Cd(OH)_2$, for the formation of this substance from its elements, $\Delta F^{\circ}_{298} = -112{,}178$; $\Delta H_{298} = -131{,}850$; and

---

[7] G. N. Lewis and Merle Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, pp. 484–485.

[8] Scheel and Heuse, ***Ann. Physik*, 4,** 40, 484 (1913).

[9] Millar, THIS JOURNAL, 50, 2653 (1928).

for the reaction $CdO + H_2O = Cd(OH)_2$, $\Delta F^\circ_{298} = -554$; $\Delta H_{298} = -1288$ (based on cell coefficients).

Thermal values for the heat of formation of cadmium oxide are Berthelot,[10] 66,400; J. Thomsen,[11] 65,780; Ditte,[12] 60,800; Mixter,[13] 5'1,000 for "amorphous" and 63,000 for crystalline, and Moose and Parr,[14] 65,200; whereas the free energy from the old cells, combined with Millar's direct entropy determination, leads to 61,950. For the hydroxide, Thomsen's value of the heat of formation from metal, oxygen and water was 65,680, which combined with Lewis and Randall's average for water, 68,270, gives 133,950 for the formation from the elements. However, Berthelot's figure for the heat of neutralization for cadmium hydroxide is 20,200 which, combined with Richards and Burgess'[15] heat of solution, 17,200, gives for the hydroxide −133,450.

The assumption of an oxide cell reaction for old cells implies that the oxide is the stable form at 25°, whereas according to the free-energy calculations, the hydroxide should be stable at this temperature. In view of this anomalous condition, no accuracy greater than perhaps 500 calories may be claimed for the free energy of the oxide.

II. Cuprous Oxide

The cuprous oxide electrode has been investigated by Allmand,[16] first against a hydrogen reference electrode in sodium or potassium hydroxide, later against the calomel electrode. Allmand found the hydrogen electrode in his solutions, to be unsatisfactory but this may have been due, in part at least, to his use of caustic alkali. Experience in this Laboratory has shown that with care the hydrogen electrode in barium hydroxide solution is fairly satisfactory. The calculated values of e.m.f. corresponding to the reaction $Cu_2O + H_2 = 2Cu + H_2O$ at 17° are given by him as 0.473 volt in 0.1 N alkali and 0.466 volt in normal alkali; part of this divergence may have been due to the uncertain liquid potentials involved in the use of the calomel reference electrode.

In the first cells of the present investigation, cuprous oxide made by dissociating a supposedly C. P. grade of cupric oxide (from nitrate) was used, with the results against the mercury oxide reference electrode of 0.4395 and 0.4479 volt, but these cells were quite unstable and maintained a steady progressive decrease of voltage. It seemed possible that this was caused by the presence of impurities in the oxide; therefore, a further

---

[10] Berthelot, *Ann. chim. phys.*, [5] 4, 189 (1875).

[11] J. Thornsen, *Ber.*, 16, 2163 (1883).

[12] A. Ditte, Bull. *soc. chim.*, [2] 16, 227 (1871).

[13] Mixter, *Am. J. Sci.*, **36**, 55 (1913); **40**, 20 (1915).

[14] J. C. Moose and S. W. Parr, THIS JOURNAL, 46, 2656 (1924).

[15] Richards and Burgess, *ibid.*, 32, 431, 1176 (1910).

[16] A. F. Allmand, J. *Chem. Soc.*, 95, 2151 (1909); 99, 840 (1911).

preparation was made by first oxidizing electrolytic copper wire in a muffle at 700° to a depth of about 0.1 mm., heating in an evacuated silica container at 1000°, and at a pressure of 0.002 mm., until no further oxygen was evolved, sealing off and permitting the contents to cool slowly. In setting up the cells, connection to the copper electrode was made through a platinum spiral upon which a dense, coherent and non-crystalline copper deposit had been electroplated.

The most satisfactory of the cells measured are shown in Table IV. Because of lack of thermostat capacity, no cells against the hydrogen reference electrode were measured at 25°. Although the cells are regarded as somewhat more satisfactory than Allmand's, previous experience had shown that the *accurate* calculation of heats of formation from cell coefficients is somewhat unsatisfactory with most oxide cells, and is barely worth while for these cells, unless gross errors exist in the thermal data, as in the previously reported case of zinc, or where it is a question of deciding between several possible cell reactions.

TABLE IV

CUPROUS OXIDE CELLS

Cell no.	Temp., °C.	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
M	24.83	HgO	0.2130	13	15	+0.45201	±0.00038
N	24.83	HgO	.1065	21	24	+ .45335	± .00085
O	24.83	HgO	.0532	6	7	+ .45184	± .00057
P	24.83	HgO	.0426	9	11	+ .45146	± .00046
Q	24.83	HgO	.0426	5	6	+ .45182	± .0011
				Average		+ .45210	± .00050
9	44.92	$H_2(p)$	.1065	6	7	− .46270	± .00030
10	44.92	$H_2(p)$	.0426	4	5	− .46298	± .00090
				Average		− .46284	

From the values of e.m.f. given in Table V, we calculate for Cu_2O, $\Delta F_{318} = -34{,}426$, $\Delta F_{298} = -34{,}672$, while Allmand's results give $\Delta F_{290} = -34{,}920$. From calculated free energies of mercuric oxide and water at 44.92, as derived from Lewis and Randall's free energy equation for these materials, the equivalent mercury oxide reference cell value of

TABLE V

CUPRIC OXIDE CELLS WITH HYDROGEN REFERENCE ELECTRODE

Cell no.	Temp., °C.	Molality $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
11	24.83	0.2120	9	10	−0.64267	±0.00018
12	24.83	.1075	6	7	− .64276	± .00019
13	24.83	.0504	3	3	− .64225	± .0010
13	24.83	.0504	5	6	− .64086	± .0021
Duplicate				Average	− .64213	± .00046
14	44.92	.2170	13	15	− .64158	± .00050
15	44.92	.1075	7	9	− .63763	± .00038
				Average	− .6396	

hydrogen cells at 44.92° is calculated to be +0.45806 volt. The value of ΔH for the formation of Cu_2O is then calculated to be —38,400 cal. Thomsen[17] gave 40,800, and Berthelot[18] 43,800. It is perhaps not to be expected that values for the heat of reaction calculated in this way from two different types of cells could give much better agreement.

Millar[19] has given a preliminary value for the entropy of cuprous oxide as 21.7 ± 1.0. Taking the entropy of copper as 8.18, in accordance with Lewis and Randall, and 24.47 for $^1/_2O_2$ as previously, ΔS for the formation of Cu_2O from its elements becomes —19.13 and ΔH is calculated from this and the free energy to be —40,375 cal., a fair substantiation of Thomsen's figure.

III. Cupric Oxide

Cupric oxide reacts with metallic copper in neutral or basic aqueous solutions, resulting in the formation of cuprous oxide. Two cells were set up, one consisting of copper in contact with CuO, with 0.0414 molal $Ba(OH)_2$, using the mercury oxide reference electrode, and the second cell Pt | CuO | 0.0414 M $Ba(OH)_2$ | Cu_2O | Pt. The first cell had an initial voltage of 0.1820 and the second of 0.1889, but the electromotive force of the first showed a rapid and continuous increase until at the end of two weeks 0.394 volt had been reached. It seemed apparent that it would ultimately increase to an amount corresponding to Cu_2O vs. HgO. The second cell was highly polarizable and showed plus and minus variations between the initial value and a maximum of about 0.244 volt.

Despite these preliminary experiments, it was decided to try the Cu | CuO electrode against a hydrogen reference electrode. It was realized that such a cell could not become completely stabilized, but might show a "steady state" value over a period of time corresponding to the reduction of CuO to Cu_2O.

Reference to Table V will show that this expectation was realized, at least in part, at 25°. At 45° the local action in the cell is so rapid that difficulty is experienced in maintaining an electroplated deposit of copper on platinum, even though copper itself (in the form of wire) was mixed with the cupric oxide. The copper oxide was of the same sample that was used in the preparation of cuprous oxide but consisted of completely oxidized wire prepared at 700°.

Assuming the cell reaction in this case to be $Cu_2O + H_2O = 2CuO + H_2$, and using the previously determined results for Cu_2O, the free energy of formation of CuO is calculated as ΔF°_{298} = —30,800, and from the integrated Gibbs-Helmholtz equation, ΔH = —38,652. Thomsen's[17] thermal value was 37,160. Millar[19] gives for the entropy of CuO, 9.75 ±

---

[17] Thomsen, J. *prakt.* Chem., [2] 12, 283 (1875).

[18] Berthelot, "Thermochemie," Vol. II, p. 317.

[19] Millar, THIS JOURNAL, 51, 215 (1929).

0.05, from which ΔS of formation is −22.90. Calculating ΔH from the cell value of free energy and the entropy as before, the result is ΔH = −37,626, a result intermediate between Thomsen's thermal value and that from cell coefficients.

IV. Stannous Oxide

Stannous oxide was prepared by boiling a solution of freshly prepared stannous chloride with sodium carbonate in the absence of air. The stannous chloride, after recrystallization, had been boiled for some time with metallic tin (shavings of special electrolytic metal) to reduce traces of stannic chloride. The original tin from which the chloride was made was of especial purity from an electrolytic refining process and contained less than 0.1% of impurity.

The stannous oxide electrode was made through a platinum spiral with an electroplated deposit of tin. The plating solution was of stannous sulfate with aloin as addition agent. In all cases except the last three cells against the mercury oxide electrode, the deposit was dense, coherent and non-crystalline. In the last three cells of this set the deposit was spongy and the cells were arranged for comparison against the same HgO electrode as the previous set.

The cells against mercury oxide showed a slow rise in voltage for about a week's time, after which they were nearly constant for the same period, but later showed a progressive decrease. It is assumed that the initial increase was caused by the slow disappearance of traces of oxygen from

TABLE VI

MEASUREMENTS OF STANNOUS OXIDE CELLS

Cell no.	Temp., °C.	Ref. electrode	Molality of $Ba(OH)_2$	E.m.f.
R1	24.83	HgO	0.2120	+1.0221
R2	24.83	HgO	.0707	+1.0205
R3	24.83	HgO	.0424	+1.0179
S1	24.83	HgO	.2120	+1.0280
S2	24.83	HgO	.0848	+1.0314
S3	24.83	HgO	.0424	+1.0328
T1	24.83	HgO	.2030	+1.0297
T2	24.83	HgO	.1075	+1.0300
T3	24.83	HgO	.0508	+1.0281
T1 (spongy tin)	24.83	HgO	.2030	+1.0298
T2 (spongy tin)	24.83	HgO	.1075	+1.0291
T3	24.83	HgO	.0508	+1.0276
	Average of last 3 sets		1.0296	±0.0011
16	44.92	H_2(p)	.2030	+0.0930
17	44.92	H_2(p)	.1015	+ .0920
			Average	+ .0925

the cells and the slow attainment of saturation with oxide, and that the final decrease resulted from the gradual spoiling of the tin surface by traces of electronegative impurities. The values given in Table VI correspond to the average for a week's period in each case at the maximum voltage attained. Despite the apparent reproducibility of the hydrogen cells, they were still showing a rise of 0.3 millivolt per day after three weeks of life, and the results are considered to be too low. This is further indicated by the calculation of free energies and heats of formation for SnO, which are

$$\left.\begin{array}{ll}\Delta F^\circ_{298} = & -61{,}332 \\ \Delta F^\circ_{318} & -60{,}054\end{array}\right\} \Delta H = -80{,}000$$

Millar[20] has found the entropy of SnO to be $S_{298} = 13.56$. Using Lewis and Randall's figure for the entropy of white tin, $S_{298} = 11.17$, and 24.47 for $^1/_2O_2$, ΔS of formation is —22.08, and ΔH from this and the measured free energy is —67,914, a good check with Andrews'[21] thermal value, 67,600.

V. Stannic Oxide

Stannic oxide was made by the oxidation of electrolytically purified tin by nitric acid, with subsequent washing, and with final calcination at 400° of the metastannic acid so formed.

Cells of this material behaved in a manner similar to the cupric oxide cells, but changed even more rapidly. In one case a cell with an initial voltage of 0.11 had changed to 0.79 volt in ten days' time. The few results recorded below represent no very definite value but rather the order of magnitude of a constantly increasing voltage, beginning at the second day of the cell's life and extending for the time recorded. After this period a more rapid rate of increase occurred. Table VII shows the results.

TABLE VII

THE STANNIC OXIDE ELECTRODE AT 44.92°

HYDROGEN REFERENCE ELECTRODE

Cell no.	Molality of $Ba(OH)_2$	No of readings	Time, days	E.m.f.	Av. dev of mean
18 Mossy Sn	0.2170	5	5	+0.1161	±0.0008
19 Coherent Sn	.2170	5	5	+ .1155	± .0010
20 Coherent Sn	.1085	2	2	+ .1148	
			Average	+ .1155	

According to the value of e.m.f., the cell reaction should have a free-energy change of $\Delta F_{318} = -10{,}660$, or —5330 cal., depending upon whether the tin is reduced to metal or the lower oxide. If the reaction was $Sn + 2H_2O = SnO_2 + 2H_2$, the free energy of formation of SnO_2

---

[20] Millar, THIS JOURNAL, 51, 207 (1929).

[21] Andrews, Phil. *Mag.*, *[3]* **32,** 321 (1848).

becomes —122,230 at 318° K., but if the cell reaction was $SnO + H_2O = SnO_2 + H_2$, $\Delta F_{318}(SnO_2) = -122,115$. It is apparent that in this case it is impossible to distinguish between the cell reactions on the basis of the evidence available. For calculation the first case is assumed. Because of lack of definiteness of electromotive force and cell reaction, further experimental work was not attempted but tentative calculations will be made.

From the specific heats of white tin and oxygen, and Lewis and Randall's entropy at 298°, the entropies at 318° are estimated as follows: $S_{318}(Sn) = 12.2$, $S_{318}(O_2) = 49.4$. Similarly, from Millar's[20] specific heat data, $S_{318}(SnO_2) = 13.3$. Then ΔS_{318} for the reaction of formation of stannic oxide is —48.3, and since $(\partial \Delta F/\partial T)_P = -\Delta S$ which varies but little with the temperature, the value of $\Delta F^\circ_{318} = -122,230$ may be corrected to 298°K. by the subtraction of 20 X 48.3 = 966 cal. Then $\Delta F_{298}(SnO_2) = -123,200$ in round numbers.

Again, calculating the entropy change of formation at 298°K. from the data, $S_{298}(Sn) = 11.18$ (Lewis and Randall), $S_{298}(O_2) = 48.94$ (as previously), $S_{298}(SnO_2) = 12.51$, $\Delta S = -47.61$. From this latter, and the estimated free energy of $-123,200$ cal., $\Delta H = -137,392$—a satisfactory check with the figures of both Mixter[22] and Andrews,[21] who gave 137,800.

The work of Fraenkel and Snipischski[23] on the reduction equilibria of stannic oxide by carbon monoxide does not permit calculation of a definitive value of free energy of stannic oxide.

VI. Lead Dioxide

The monoxide of lead electrode has been investigated by Smith and Woods,[5] who found for the free energy of formation of PbO, $\Delta F^\circ_{298} = -45,050$ cal. Lead dioxide, lead sesquioxide and red lead have been studied by Glasstone,[24] who gave for the Pt | PbO, PbO_2 N–NaOH electrode potential 0.27 volt, and concluded that PbO and PbO_2 combine in the presence of N alkali to give Pb_3O_4.

In the present work we wished to ascertain whether these results were duplicable in barium hydroxide electrolyte. Lead dioxide was made electrolytically in a lead perchlorate solution which was hot and strongly acid. The lead electrode was made by deposition from a lead perchlorate solution with peptone as addition agent. Comparisons of the Pb | PbO_2 | $Ba(OH)_2$ electrode with the mercury oxide and hydrogen electrode are given in Table VIII.

If the cell reaction be assumed to be the reduction of lead dioxide to

---

[22] Mixter, *Silliman's* J., [4] 27, 231 (1909).

[23] Fraenkel and Snipischski, *Z. anorg. allgem. Chem.*, 125, 235 (1923).

[24] Glasstone, *J. Chem. Soc.*, 121, 1456 (1922).

TABLE VIII

MEASUREMENTS ON LEAD DIOXIDE CELLS

Cell no.	Ref. electrode	Temp., °C.	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
U	HgO	24.83	0.1015	10	12	+0.69140	±0.00037
V	HgO	24.83	.0508	9	11	+ .69148	± .00043
				Average		– .69144	
21	H_2(p)	44.92	.2030	7	8	– .1983	± .0009
22	H_2(p)	44.92	.1085	6	7	– .1924	± .0003
23	H_2(p)	44.92	.0543	6	7	– .1967	± .0009
24	H_2(p)	44.92	.2170	4	5	– .1977	± .0011
				Average		– .1962	

monoxide, these voltages lead to a free energy of the dioxide of approximately —90,000 cal., but if the cell reaction is assumed to be the complete reduction of the dioxide, the order of magnitude of the calculated free energy of the dioxide is not changed. Calculations from either type of cell are moderately concordant and it is obvious that the cell reaction could not involve a reduction of PbO_2. If, however, it is assumed that the cell reaction may be only the formation or reduction of monoxide, the free energy of formation of the monoxide calculated from the observed voltage is $\Delta F^\circ_{298} = -45{,}717$. This figure is sufficiently close to Smith and Woods' result of —45,050 to justify belief that the actual cell reaction was principally lead monoxide formation.

It is of interest to calculate for copper, tin and lead the free-energy change resulting from the reduction of the higher to lower oxide by the metal at 25°. The free energies used for copper and tin are taken from this work, but for lead dioxide the figure calculated by Millar[20] and for lead monoxide the result of Smith and Woods are used.

$$Cu + CuO = Cu_2O$$
$$-30{,}800 \qquad -34{,}672 \qquad \Delta F = -3872$$
$$Sn + SnO_2 = 2SnO$$
$$-123{,}200 \qquad 2 \times (-61{,}332) \qquad \Delta F = +536$$
$$Pb + PbO_2 = 2PbO$$
$$-52{,}010 \qquad 2 \times (-45{,}050) \qquad \Delta F = -38{,}090$$

The large negative free-energy change for the lead reaction is adequate explanation for the disappearance of the dioxide in contact with the lead electrode, and the rapid degeneration of the cell as made with dioxide to give only monoxide reactions. The degeneration of the cupric oxide cells noted in an earlier part of this paper is consistent with the calculation showing that cupric oxide is not stable in contact with copper, and in this case the reaction occurring was actually the transformation from one to the other oxide. Stannous oxide has been described by T. Maeda[25] as unstable with respect to tin and stannic oxide at 700–950°. The small calculated positive value of the reaction for tin as written above accounts

[25] T. Maeda, *Bull. Japan Inst. Phys. Chem. Research,* 2,350 (1923).

for the lack of definiteness in the tin cells, since the formation or reduction of either oxide could not be expected to take place exclusively.

It is not probable that a lead monoxide electrode made up originally with lead dioxide could give results of sufficient accuracy to serve as criticism of Smith and Woods' figures, and their result is undoubtedly the accurate one.

VII. Comment Concerning Oxide Electrodes

In this work it was found that cells involving oxide electrodes were highly polarizable and very sensitive to the presence of traces of electronegative impurities in the oxide material and electrolyte. Much of the difficulty with oxide or electrolyte containing more electronegative elements as impurity and resulting in rapid deterioration of the cells because of strong local action is readily eliminated by treating the oxide in suspension in the electrolyte with turnings of the pure metal in question for some time before use (preferably at a boiling temperature). Such turnings added to the cell contents are not entirely satisfactory, since the electrodeposited metal of the electrode proper usually acts preferentially in replacing the electronegative elements. In spite of such precautions, it was found impossible to produce cells which were *permanently* stable, although it was often possible to produce cells having constant e.m.f.'s for several weeks. Because of the inherent variations and polarizability of the cells, the temperature coefficient of oxide cells is usually difficult to determine with sufficient accuracy to give satisfactory thermal data.

Entropy calculations have been of great use in determining the cell reaction and furnishing assurance of the validity of the measurements. It is thought that free-energy determinations combined with entropy values will make possible the calculation of heats of formation, in many cases much more accurately than any possible direct determination. Because of the difficulty of obtaining thermal data from these cells, the selection of the cell reaction is uncertain in some cases; for this reason the results have been found acceptable only when substantiated by check with other independent methods, especially entropy determinations.

TABLE IX

SUMMARY OF MEASUREMENTS AND CALCULATIONS

Subs.	ΔF°_{298} of formation	S_{298} (Millar)	ΔH_{298} (formation) from cell coef.	ΔH_{298} (formation) from ΔF and S
CdO	$-55{,}064 \pm 500$	13.17 ± 0.1	$-62{,}305 \pm 500$	$-61{,}950 \pm 500$
$Cd(OH)_2$	$-112{,}178 \pm 500$	....	$-131{,}850 \pm 500$	....
Cu_2O	$-34{,}672 \pm 200$	21.7 ± 1.0	$-38{,}400 \pm 2000$	$-40{,}375 \pm 400$
CuO	$-30{,}800 \pm 200$	9.75 ± 0.05	$-38{,}652 \pm 1000$	$-37{,}626 \pm 200$
SnO	$-61{,}332 \pm 300$	13.56	$-80{,}000 \pm 15000$	$-67{,}914 \pm 300$
SnO_2	$-123{,}200 \pm 400$	13.51	....	$-137{,}400 \pm 400$

Summary

1. Oxide electrodes of cadmium oxide, cuprous and cupric oxide, stannous and stannic oxide and lead dioxide have been compared to the hydrogen or mercuric oxide electrode in barium hydroxide solutions.

2. Free energies of formation from these results and calculated heats of formation are summarized in Table IX.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITIES AT LOW TEMPEMTURES OF THE OXIDES OF TIN AND LEAD[1]

BY RUSSELL W. MILLAR[2]

RECEIVED OCTOBER 8, 1928 PUBLISHED JANUARY 8, 1929

In continuation of the general program of determination and compilation of thermal and equilibrium data concerning the oxides and sulfides of metals, the heat capacities of SnO, SnO_2, Pb_3O_4 and PbO_2 have been measured from about 70°K. to room temperature. The method and apparatus employed were those previously used by the author.[3]

Materials.—The stannous oxide was made by the precipitation of stannous hydroxide with ammonia from a boiling solution of pure stannous chloride. Dehydration was accomplished by boiling the solution. The addition of a few crystals of stannous chloride, as recommended by Ditte,[4] hastened the reaction. The oxide was at first dark red but soon changed to the stable bluish black modification. It was cooled, filtered, washed with cold water and dried *in vacuo* over fused potassium hydroxide to constant analysis. Air was excluded as well as possible during filtration and washing. Titration with standard iodine solution of two samples dissolved in hydrochloric acid showed 98.0% of SnO. The impurity was probably SnO_2. Metallic-tin, determined by reduction with hydrogen, was 87.36 to 87.21%, whereas the theoretical percentage is 88.12.

Stannic oxide was made by the action of dilute nitric acid on pure electrolytic tin. The material, when washed and ignited at 400°, was analyzed by reduction with hydrogen. Two determinations gave 99.84 and 99.73% of the theoretical amount of tin.

Lead dioxide was prepared by the electrolysis of an acid solution of lead nitrate, according to the method of Palmaer.6 Lead carbonate was added to maintain the lead-ion concentration and to prevent the hydrogen-ion concentration from rising. Crystalline lead was formed at the cathode and dense plates of lead dioxide, which attained a thickness of 2–3 mm., at the anode. The product was ground to pass a 14-mesh screen, washed with boiling water until the washings showed no trace of nitrate and dried at 120°. Analysis by oxidation of hydrochloric acid, absorption of the chlorine evolved

---

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate chemist, Pacific Experiment Station, Berkeley, California.

[3] Millar, THIS JOURNAL, 50, 1875 (1928).

[4] Ditte, *Compt. rend.*, 94, 792, 864 (1882).

[5] Palmaer, *Medd.* Kgl. *Vetenskapsakad, Nobelinst.*, *5*, 1 (1919).

in potassium iodide solution, and titration of the iodine with standard thiosulfate showed 99.8, 99.2 and 99.6% of the theoretical amount of active oxygen.

Lead orthoplumbate, or minium, was prepared by decomposition of electrolytic lead dioxide in a stirred bath of molten potassium nitrate at 460°, according to Milbauer.[6] The salt was washed out and the product was dried at 120°. Analysis by the method used for lead dioxide indicated only 98.7, 96.1, 96.5, 96.5 and 97.2% of the theoretical quantity of active oxygen. Reduction by hydrogen showed 90.62% lead, whereas the theoretical percentage is 90.66. Probably decomposition of the dioxide was carried too far by excessive heating of the sides of the nitrate bath, but an impurity of considerable lead monoxide cannot be serious, since the heat capacity of lead orthoplumbate is only slightly more than three times that of the monoxide throughout the range of temperature of the measurements.

In the following tables heat capacities are expressed in gram calories (15°) per mole. One calorie is equal to 4.185 absolute joules. The calculations were made on the basis of O = 16, Sn = 118.7 and Pb = 207.20.

TABLE I

THE MOLAL HEAT CAPACITY OF SnO

T, °K.	69.6	73.0	81.7	93.3	108.1	125.0	140.8	156.9
C_p	4.067	4.300	4.910	5.432	6.251	6.975	7.594	8.145
T, °K.	181.7	193.5	209.7	230.2	251.3	268.3	284.3	292.5
C_p	8.856	9.172	9.536	9.917	10.17	10.24	10.51	10.52

TABLE II

THE MOLAL HEAT CAPACITY OF SnO_2

T, °K.	71.8	75.2	79.3	84.8	93.8	103.6	118.2	126.0	
C_p	3.087	3.323	3.619	3.995	4.532	5.242	6.165	6.621	
T, °K.	142.2	154.6	181.8	202.7	215.5	271.6	273.4	287.2	289.4
C_p	7.442	8.103	9.319	10.18	11.05	12.02	12.15	12.30	12.41

TABLE III

THE MOLAL HEAT CAPACITY OF Pb_3O_4

T, °K.	71.5	78.5	85.6	100.1	111.7	127.1	138.6	151.3	172.1
C_p	16.65	17.82	18.81	20.55	22.33	24.29	25.82	27.08	28.77
T, °K.	187.4	208.8	227.1	247.1	259.8	266.2	278.2	292.6	
C_p	30.34	31.66	32.73	34.24	33.00	34.44	34.37	34.46	

Owing to its low apparent density, only about 0.3 mole of lead orthoplumbate could be loaded into the calorimeter, so that the empty calorimeter had more heat capacity than the sample. The result was a loss in accuracy. Usually the heat capacity of the sample was 1.5 to 4 times that of the empty calorimeter. The large errors in Points 13, 14 and 15 can be explained only by poor contacts in the potentiometer switches, which were causing trouble at the time.

An uncertainty at the lower end of the temperature scale caused inaccuracy in the calculations for Points 1, 2 and 3 in Table IV.

---

[6] Milbauer, *Chem.-Ztg.*, 38,477.559.566.587 (1914).

TABLE IV

THE MOLAL HEAT CAPACITY OF PbO_2

T, °K.	69.9	73.1	84.5	89.8	98.9	111.6	126.0	140.7	151.8	166.9
C_p	5.430	5.688	6.345	6.866	7.484	8.337	9.160	9.971	10.46	11.23
T, °K.	183.4	198.4	212.9	227.9	242.0	261.6	270.5	298.1	297.2	
C_p	11.94	12.72	13.11	13.50	13.95	14.60	14.83	15.42	15.43	

As before, the entropy of the oxide at 25° was calculated by graphical integration in the range covered by the data, using the relation

$$S_{298} - S_T = \int_T^{298} C_p \mathrm{d} \ln T$$

and by extrapolation to the absolute zero by means of combinations of Debye and Einstein functions. The following equations indicate the values of $\beta\nu$ used in these functions, denoted by $D(\beta\nu/T)$ and $E(\beta\nu/T)$, for the substances named, and the maximum temperatures for which the combinations of theoretical curves reproduce the experimental values of C_p.

SnO,	$D\left(\frac{215}{T}\right) + E\left(\frac{494}{T}\right)$	0.5% to 178°K.
SnO_2,	$D\left(\frac{305}{T}\right) + E\left(\frac{487}{T}\right) + E\left(\frac{968}{T}\right)$	0.5% to 200°K.
Pb_3O_4,	$3D\left(\frac{119}{T}\right) + E(f)$	......
PbO_2,	$D\left(\frac{183}{T}\right) + E\left(\frac{342}{T}\right)$	0.5% to 94°K.

The curve for Pb_3O_4 follows closely that of 3PbO drawn from the data of Nernst and Schwers[7] and of Russell.[8] The difference decreases rapidly with decreasing temperature, and probably does not reverse sign, so that, at low temperatures, the two curves follow the same Debye curve. Although better agreement with C_v, if sufficient data for the calculation of this quantity existed, could doubtless be obtained if more complicated combinations of these two functions were devised, nothing would be gained, since the extrapolation gives the entropy with only a slight error in any case.

The entropies of these oxides at 25° are: SnO, 13.56; SnO_2, 12.51; Pb_3O_4, **60.53;** PbO_2, 18.27.

In order to calculate the free energy according to the equation

$$AF = \Delta H - T\Delta S \tag{1}$$

for the reaction metal + oxygen = oxide, we must know the entropies of metallic tin, lead and of oxygen. From Bronsted's[9] data, Lewis, Gibson and Latimer[10] have calculated for Sn (white), $S^\circ_{298} = 11.17$, and

---

[7] Nernst and Schwers, *Sitzb. preuss. Akad. Wiss.*, 355 (1914).

[8] Russell, *Physik. Z.*, 13, 59 (1912).

[9] Bronsted, *Z. physik. Chem.*, 88, 479 (1914).

[10] Lewis, Gibson and Latimer, THIS JOURNAL, 44, 1008 (1922).

from those of Griffiths and Griffiths[11] for Pb, $S^{\circ}_{298} = 15.53$. As before, for O_2, $S^{\circ}_{298} = 49.2$.

Stannous Oxide.—No reliable values of the heats of formation of the oxides of tin exist. For the reaction $Sn(s) + 1/2O_2(g) \doteq SnO(s)$, Mixter[12] gives $AH = -66{,}800$, Andrews[13] $-67{,}600$, Delephine and Hallopean[14] $-70{,}700$, and G. Chaudron[15] $-69{,}000$. The results of measurements made in this Laboratory of the e.m.f. of cells, which will soon be published, give an accurate value of the free energy of stannous oxide, from which will be calculated a value of its heat of formation more accurate than any of the above.

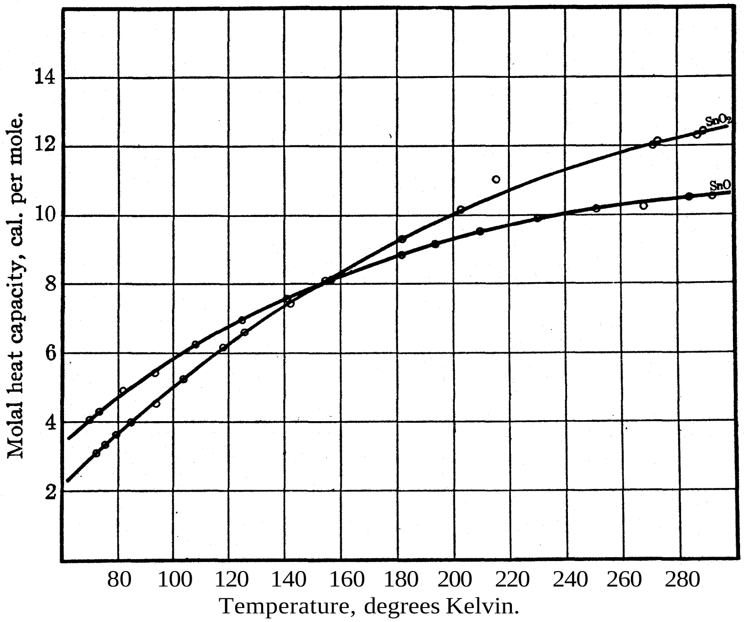


Fig. 1.—The molal heat capacities of SnO and SnO_2.

Stannic Oxide.—For the reaction Sn (white) + $O_2(g) = SnO_2(s)$, Mixter gives $\Delta H = -137{,}800$; Andrews $-137{,}800$; Moose and Parr[16] $-138{,}200$; and Maeda[17] $-130{,}260$. Mixter's value, $-137{,}800$, is probably but little in error. From the entropies of white tin, oxygen and stannic oxide, $\Delta S^{\circ}_{298} = -47.86$ and, finally, for $SnO_2(s)$, $\Delta F^{\circ}_{298} = -123{,}540$.

Lead Monoxide.—For the reaction $Pb(s) + 1/2O_2(g) = PbO(s)$,

---

[11] Grifiiths and Griffiths, *Proc. Roy. Soc., London,* **90A,** 557 (1914).

[12] Mixter, *Am. J. Sci.,* [4] 27, 229 (1909).

[13] Andrews, *Phil. Mag.,* [3] 32, 321 (1848).

[14] Delephine and Hallopean, *Compt. rend.,* 129, 600 (1899).

[15] Chaudron, *Ann. chim. phys.,* [9] 16, 220 (1921).

[16] Moose and Parr, This Journal, 46, 2656 (1924).

[17] Maeda, *Bull. Japan Inst. Phys. Chem. Research,* 2, 350 (1923).

G. Chaudron[15] gives $\Delta H = -50{,}200$, Treadwell[18] $-50{,}400$, Berthelot[19] $-50{,}800$, Thomsen[20] $-50{,}300$, Gunther[Zl] $-52{,}900$ and Smith and Woods[22] $-52{,}360$. With the exception of the last two, these values are exceptionally concordant and would ordinarily be accepted, but the cells of Smith and Woods,[22] which were of the form Pb(s) + PbO(red) | $Ba(OH)_2$ soln. | H_2(g) were exceptionally reproducible at both 25 and 45°. Günther, who determined accurately the heat of formation of lead chloride by means of cell measurements, concluded that Thomsen's value for that quantity

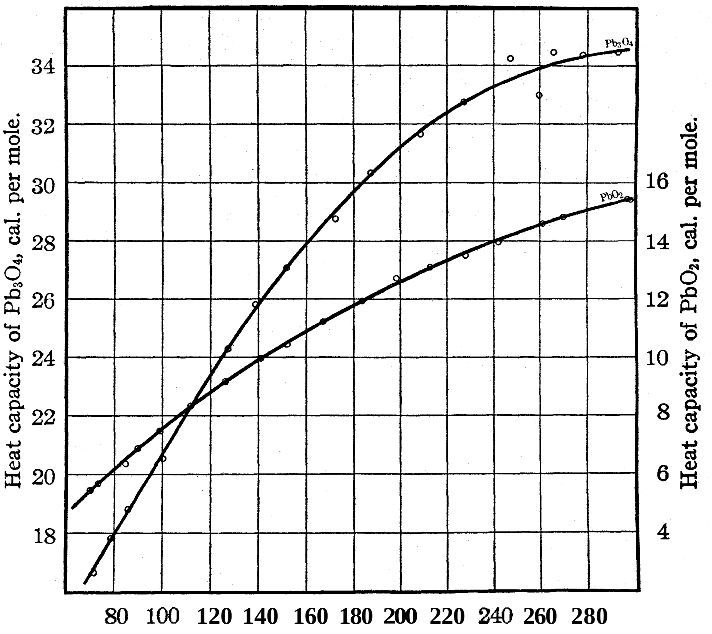


Fig. 2.—The molal heat capacities of Pb_3O_4 and PbO_2.

was too large by 2600 calories, and recalculated the latter's data for lead monoxide on that basis. Since Smith and Woods are the only investigators who definitely state that they used the red, tetragonal form, which is the stable one at room temperature, instead of the yellow, orthorhombic form, and since their measurements are undoubtedly accurate, their values of the free energy and the heat of formation are accepted and are quoted here for later reference.

$$\text{Pb(s)} + 1/2\text{O}_2\text{(g)} = \text{PbO(red)};\quad \Delta F^\circ_{298} = -45{,}050;\quad \Delta H_{298} = -52{,}360 \qquad (2)$$

---

[18] Treadwell, Z. *Elektrochem.*, 22,414 (1916).

[19] Berthelot, Ann. *chim. phys.*, [4] 30, 191 (1873).

[20] Thomsen, "Thermochemische Untersuchung," Leipzig, 3,329 (1883).

[21] Giinther, Z. *Elekfrochem.*,23, 197 (1927).

[22] Smith and Woods, THIS JOURNAL, 45,2632 (1923).

Randall and Spencer,[23] from measurements of the solubility of red and yellow lead monoxide in solution of sodium hydroxide, have calculated the difference in free energy of the two forms

$$\text{PbO(yellow)} = \text{PbO(red)};\quad \Delta F_{298} = -163 \qquad (3)$$

Lead Dioxide.—For the reaction $PbO(s) + 1/2O_2(g) = PbO_2(s)$, Tscheltzow[24] gives $\Delta H = -12{,}140$, which added to Equation 2 gives for the reaction $Pb(s) + O_2(g) = PbO_2(s)$, $\Delta H = -64{,}500$. Mixter[25] gives $-65{,}600$.

Glasstone,[26] from cell measurements, has calculated the free energy changes at 17° of several reactions involving the oxides of lead. Apparently his lead monoxide was the red form. A recalculation of his two most reliable sets of measurements gives

$$PbO_2(s) + H_2(g) = \text{PbO(red)} + H_2O(l);\quad \Delta F^\circ_{298} = -49{,}600 \qquad (4)$$

$$3PbO_2(s) + 2H_2(g) = Pb_3O_4(s) + 2H_2O(l);\quad \Delta F^\circ_{298} = -104{,}360 \qquad (5)$$

From Equations 2 and 4 and the free energy of water

$$H_2(g) + 1/2O_2(g) = H_2O(l);\quad \Delta F^\circ_{298} = -56{,}560 \qquad (6)$$

given by Lewis and Randall[27]

$$Pb(s) + O_2(g) = PbO_2(s);\quad \Delta F^\circ_{298} = -52{,}010 \qquad (7)$$

Wescott,[28] from determinations of the equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + 2H_2O = PbO_2(s) + 4HCl(soln.)$ and the free energy of lead chloride, calculated for $Pb(s) + O_2(g) = PbO_2(s)$, $\Delta F^\circ_{298} = -52{,}330$, but he used an old value, $-56{,}620$, as the free energy of liquid water. When the more recent value given in Equation 6 is used, his results give $-52{,}210$ for the free energy of lead dioxide. The good agreement with Glasstone's value given in Equation 7 must, however, be considered as fortuitous, since the activity of the hydrochloric acid in Wescott's solution was somewhat uncertain. By combining Equations 1 and 7 with the entropies of lead, oxygen and lead dioxide, the heat of formation of lead dioxide can be calculated:

$$Pb(s) + O_2 = PbO_2(s);\quad \Delta H_{298} = -65{,}960 \qquad (8)$$

in fair agreement with Mixter's value.

Lead Orthoplumbate.—By combining Equations 2, 4, 5 and 6

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\quad \Delta F^\circ_{298} = -147{,}270 \qquad (9)$$

a value which can be compared with one calculated from careful measurements of the decomposition pressure of lead orthoplumbate by Reinders

---

[23] Randall and Spencer, THIS JOURNAL, 50, 1572 (1928).

[24] Tscheltzow, *Compt. rend.*, 100, 1458 (1885).

[25] Mixter, *Am. J. Sci.*, [4] 27, 396 (1909).

[26] Glasstone, *J. Chem. Soc.*, 121, 1456, 1469 (1922).

[27] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 485.

[28] Wescott, THIS JOURNAL, 42, 1335 (1920).

and Hamburger.[29] They showed that, at the temperatures of their measurements, yellow lead monoxide was formed, and that it did not form solid solutions with the lead orthoplumbate. Their data have been treated by the method described by Lewis and Randall,[30] whose equations and symbols will be used in what follows. The reaction is $2Pb_3O_4(s) = 6PbO(yellow) + O_2$. Reinders and Hamburger represent their results accurately by the equation

$$\log p_{mm.} = -\frac{35{,}926}{4.5717T} + 11.8976$$

where it is evident that they have used for the gas constant, R = 4.571/2.303 instead of 1.9885, the value accepted here. If 1.9885 is used, their data may be equally well represented by

$$\log p_{,,} = -\frac{35{,}987}{4.57787T} + 11.8976$$

Calculation by means of the approximation $d \ln p/d(1/T) = -\Delta H/R$ gives for their reaction, $\Delta H = -35{,}987$. Heat capacity equations for the substances involved are now required in order to calculate ΔH_0.

From the determinations of Regnault[31] and of Magnus[32] the heat capacity of lead monoxide is 11.4 at 330°K. and 11.7 at 417°K., whence for PbO, $C_p = 10.26 + 0.0034T$. At room temperature the heat capacity of lead orthoplumbate is 3.06 times that of lead monoxide. Assuming that this ratio holds through the region of Reinders and Hamburger's measurements, for Pb_3O_4, $C_p = 31.41 + 0.0106T$. For oxygen Lewis and Randall[33] give O_2, $C_p = 6.50 + 0.0010T$. For the decomposition of two moles of lead orthoplumbate, $\Delta C_p = 5.24 + 0.0005T$. Taking, at the average temperature of the measurements, $\Delta H_{823} = 35{,}987$, ΔH_0 becomes 31,505. The standard free energy change at the temperature of each of the 16 experiments was calculated by means of the equation $AF^{\circ} = -RT \ln P$, where P is the experimentally determined pressure of the oxygen in atmospheres. By substitution of these values of ΔF°, ΔH_0, and the coefficients of the equation for ΔC_p in the free energy equation in the usual way, 16 values of the integration constant I were calculated which varied from —0.77 to —0.31, most of them being grouped closely about the average, I = —0.52. Then for

$$2Pb_3O_4(s) = 6PbO(yellow) + O_2;\quad AF^{\circ} = 31{,}505 - 5.24T \ln T - 0.00025T^2 - 0.52T;$$
$$\Delta F^{\circ}_{298} = 22{,}430;\quad \Delta H_{298} = 33{,}090 \qquad (10)$$

From Equations 1 and 10, $AS''_{„} = 35.76$, and by the use of the entropies of Pb_3O_4 and O_2, PbO(yellow), $S^{\circ}_{298} = 17.94$.

---

[29] Reinders and Hamburger, *Z. anorg. Chem.*, 89, 71 (1914).

[30] Lewis and Randall, ref. 27, p. 173.

[31] Regnault, *Ann. chim. phys.*, [3] 1, 129 (1841).

[32] Magnus, *Physik. Z.*, 14, 5 (1913).

[33] Lewis and Randall, ref. 27, p. 80.

Combining Equations 2, 3 and 10

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\ \Delta F^{\circ}_{298} = -145{,}870$$

and with the entropies of Pb_3O_4, Pb and O_2

$$\Delta H_{298} = -171{,}050 \qquad (11)$$

On returning to Equations 10 and 11, it may be noted that

$$Pb(s) + 1/2O_2 = PbO(\text{yellow});\ \Delta H_{298} = -51{,}500$$

and with 2

$$PbO(\text{yellow}) = PbO(\text{red});\ \Delta H_{298} = -860;\ \Delta S^{\circ}_{298} = -2.35 \qquad (12)$$

From Equations 1 and 2, PbO(red), $S^{\circ}_{298} = 15.62$. Smith and Woods in their paper noted the large discrepancy between their value of the entropy of red lead monoxide and the value of the entropy of lead monoxide, 16.3, which Lewis and Randall[34] calculated from measurements of its heat capacity by Nernst and Schwers.[7] The writer has recalculated the entropy from the same data and obtained 16.41, whereas Miething,[35] using the same data, obtained 17.04. Nernst and Schwers, although they say nothing concerning their sample, probably used the yellow form.

The entropy of yellow lead monoxide which was calculated from Reinders and Hamburger's results, 17.94, is undoubtedly too high, due probably to the assumptions regarding the heat capacities of lead monoxide and orthoplumbate above room temperature. For the present, then, the free energy of lead orthoplumbate which was calculated from Glasstone's data will be accepted, together with the corresponding heat of formation calculated from the entropies of this substance and of lead and oxygen. Thus

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\ \Delta F^{\circ}_{298} = -147{,}270;\ \Delta H_{298} = -172{,}440$$

Likewise, from Equations 2 and 3, the entropy of yellow lead monoxide, 16.41, and the entropies of lead and oxygen

$$Pb(s) + 1/2O_2(g) = PbO(\text{yellow});\ \Delta F^{\circ}_{298} = -44{,}887;\ \Delta H_{298} = -51{,}960$$

Summary

The heat capacities of stannous and stannic oxide, lead dioxide and lead orthoplumbate have been determined from 70 to 300°K. and their entropies at 25° have been calculated.

The following table contains the results of calculations from these data and others found in the literature.

	S°_{298}	ΔF°_{298}	ΔH_{298}
$SnO(s)$	13.56	....	....
$SnO_2(s)$	12.51	−123.540	−137,800
PbO(red)	15.62	− 45,050	− 52,360
PbO(yellow)	16.4	− 44,887	− 51,960
$Pb_3O_4(s)$	60.53	−147,270	−172,440
$PbO_2(s)$	18.27	− 52,010	− 65,960

BERKELEY, CALIFORNIA

---

[34] Lewis and Randall, ref. 27, p. 498.

[35] Miething, *Abhand. deut. Bunsen-Ges.*, No. 9, 1920.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF "FERROUS OXIDE," MAGNETITE AND CUPROUS AND CUPRIC OXIDES[1]

BY RUSSELL W. MILLAR[2]

RECEIVED OCTOBER 8, 1928 PUBLISHED JANUARY 8, 1929

The thermodynamic properties of the important and interesting substances "ferrous oxide," magnetite and cuprous and cupric oxides, have been the subject of an enormous amount of experimental investigations and of an even greater amount of speculation. No attempt will be made here to review the accumulated data relating to the equilibria of these oxides with oxygen and the corresponding metals; most of the data are only approximations which fail to agree. The measurements presented here leave something to be desired with regard to ferrous oxide, which has never yet been prepared pure in quantities greater than a gram, and with regard to the entropy of cuprous oxide, which has at the lowest temperatures at which measurements were made, 75°K., the abnormally high heat capacity of over 8 calories per mole.

Materials.—A sample of crude ferrous oxide, kindly supplied by the Fixed Nitrogen Research Laboratory, was separated magnetically according to the method of Wyckoff and Crittenden.[3] The analysis, according to the method of Sims and Larsen,[4] which agrees with theirs as well as could be expected, was as follows: total iron, 77.24%; free iron, 0.80%; ferrous iron, 68.46%; and ferric iron (by difference), 7.98%. If we assume that all of the ferric oxide is combined with ferrous oxide as magnetite, Fe_3O_4, the material contained free iron, 0.80%; ferrous oxide, 83.05%; and magnetite 16.15%. Although Wyckoff and Crittenden conclude, as a result of their crystallographic measurements, that the purity of the material was much greater, large errors in the analysis do not seem probable in view of the care used to prevent oxidation during dissolution of the sample.

Although many attempts to secure pure ferrous oxide have been made, none has been successful, if we except those of Hilpert and Beyer,[5] Wohler and Balz,[6] and Wohler and Günther,[7] who prepared samples of 98–100% purity, but only in quantities of less than 1 g. Attempts to produce larger quantities are now being made in this Laboratory, but so far with indifferent

---

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate chemist, Pacific Experiment Station, Berkeley, California.

[3] Wyckoff and Crittenden, THIS JOURNAL, 47, 2876 (1925).

[4] Sims and Larsen, *Ind. Eng. Chem.*, 17, 86 (1925).

[5] Hilpert and Beyer, *Ber.*, 44, 1608 (1911).

[6] Wohler and Balz, *Z. Elektrochem.*, 27, 406 (1921).

[7] Wohler and Günther, *ibid.*, 29, 276 (1923).

success. One embarrassing characteristic, as found by Chaudron,[8] is that the reaction 4FeO = Fe + Fe_3O_4 tends to take place below 570°, so that all preparations made above that temperature must be cooled to room temperature as rapidly as possible. Such a procedure is objectionable because a quenched material has internal strains which cause variations from the thermodynamic properties of the stable form.

The magnetite, from the deposit at Mineville, N. Y., was kindly lent for these measurements by Dr. Sosman of the Geophysical Laboratory of the Carnegie Institution of Washington, The ore was similar to that used by Sosman and Hostetter,[9] whose analysis was: Fe_3O_4, 99.0%; Fe_2O_3, 0.63%; and impurities, largely quartz, 0.37%. A correction was made for the heat capacity of the quartz.

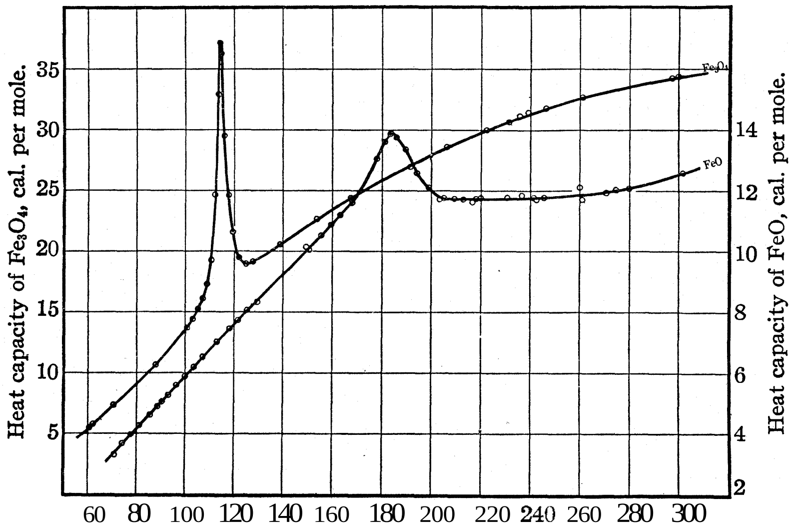


Fig. I—The molal heat capacities of FeO and Fe_3O_4.

The cupric oxide was made by heating No. 28 copper wire in a muffle at 700° until oxidation was apparently complete. Analysis by reduction with hydrogen showed 79.90 and 79.91% copper, whereas the theoretical percentage is 79.89; this corresponds to 0.60% cuprous oxide, but the sample was completely soluble in 4% sulfuric acid without the deposition of metallic copper. The wire was probably completely converted to cupric oxide, but contained the residual impurities of the original copper.

The cuprous oxide was prepared from the cupric oxide by decomposition at about 0.002 mm. pressure in a silica tube, as described by Maier.[10]

[8] Chaudron, *Ann. chim. phys.*, [9] 16,271 (1921).

[9] Sosman and Hostetter, THIS JOURNAL, 38,812 (1916).

[10] Maier, *ibid.*, 51, 194 (1929).

After heating at about 700° until a layer of cuprous oxide, which does not seriously attack fused silica ware below 1100°, had been formed on the outside, the temperature was raised to 1000° and maintained until no more oxygen was evolved. Reduction by hydrogen showed 88.82% of copper, which is the theoretical proportion.

In calculating the heat capacity of the ferrous oxide, it was assumed that the specific heat of the sample was the same as that of pure ferrous oxide. The magnetite and iron are in solid solution in the ferrous oxide, as is shown by the lack of magnetism of the sample and by the normal course of the heat capacity curve near 114°K., where the curve for pure magnetite shows a sharp maximum. Consequently a correction could not be made for the magnetite as if it were a separate phase, and although our knowledge of the properties of pure ferrous oxide may be none the greater, the procedure adopted seemed the only feasible one. Moreover, it seems improbable that the heat capacity of pure ferrous oxide at 25° is as high as 12.5, the value given, since the heat capacity of manganous oxide, 10.30, is very nearly that predicted by Kopp's law, 10.2.

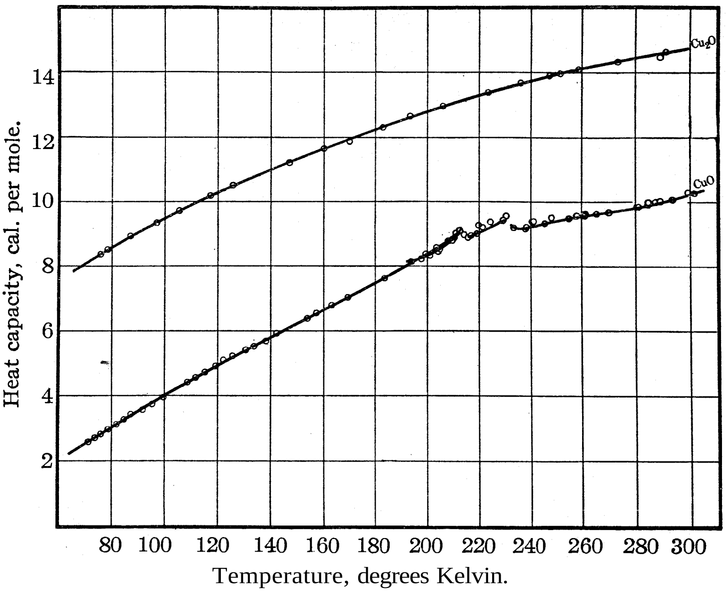


Fig. 2.—The molal heat capacities of Cu_2O and CuO.

In the following tables, heat capacities are expressed in gram calories (15°) per mole. One calorie is equal to 4.185 absolute joules. The calculations were made on the basis of O = 16, Cu = 63.57 and Fe = 55.84.

The measurements of the heat capacity of magnetite agree with those of Parks and Kelley[11] at the lowest temperatures, but gradually become

---

[11] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

TABLE I

THE MOLAL HEAT CAPACITY OF "FERROUS OXIDE," *viz.*, THE HEAT CAPACITY OF 71.84 G. OF THE SAMPLE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	301.8	12.56	17	125.4	8.036	33	177.8	13.02
2	70.7	3.296	18	129.5	8.318	34	181.0	13.59
3	74.1	3.662	19	150.6	10.04	35	183.2	13 86
4	77.5	3.952	20	155.3	10.51	36	185.7	13.75
5	81.0	4.254	21	159.5	10.87	37	189.5	13.35
6	85.5	4.594	22	163.4	11.19	38	194.1	12.57
7	88.5	4.882	23	168.0	11.59	39	198.8	12.09
8	90.1	5.042	24	205.0	11.75	40	203.3	11.70
9	93.0	5.252	25	209.3	11.73	41	217.9	11.72
10	96.3	5.574	26	212.8	11.70	42	230.5	11.77
11	99.8	5.866	27	216.5	11.60	43	236.5	11.84
12	103.4	6.174	28	219.9	11.75	44	241.3	11.77
13	107.1	6.488	29	242.5	11.70	45	261.0	11.69
14	113.0	6.984	30	245.5	11.76	46	270.7	11.93
15	118.2	7.440	31	260.0	12.09	47	274.6	12.02
16	121.6	7.720	32	149.3	10.12	48	279.8	12 09

TABLE II

THE MOLAL HEAT CAPACITY OF MAGNETITE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	297.3	34.28	12	110.4	19.25	23	153.7	22.63
2	299.7	34.39	13	112.0	24.62	24	167.5	24.36
3	60.5	5.495	14	113.6	32.92	25	191.4	26.98
4	62.0	5.771	15	114.7	36.27	26	206.2	28.59
5	70.5	7.331	16	115.9	29.49	27	222.1	30.00
6	87.6	10.63	17	117.6	24.58	28	235.7	31.18
7	100.7	13.67	18	119.4	21.52	29	239.2	31.45
8	103.0	14.38	19	121.8	19.48	30	231.3	30.67
9	105.1	15.20	20	124.8	18.95	31	246.0	31.81
10	107.0	16.09	21	127.5	19.16	32	261.1	32.68
11	108.8	17.27	22	138.9	20.53			

Fe_3O_4 (110°K.) = Fe_3O_4 (125°K.). $\Delta H = 361.4$

TABLE III

THE MOLAL HEAT CAPACITY OF CUPROUS OXIDE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K	C_p
1	147.0	11.22	8	236.1	13.70	15	75.9	8.366
2	159.9	11.66	9	247.6	13.93	16	78.4	8.519
3	170.0	11.89	10	259.0	14.12	17	87.0	8.935
4	182.9	12.32	11	252.1	13.98	18	96.9	9.355
5	192.9	12.67	12	273.5	14.36	19	105.3	9.721
6	206.1	12.98	13	289.1	14.50	20	117.0	10.18
7	223.5	13.40	14	291.0	14.66	21	125.6	10.51

less as the temperature rises, finally reaching a difference of 5.8% at 25°. Part of the difference is accounted for by a correction for the **quartz** in

TABLE IV

THE MOLAL HEAT CAPACITY OF CUPRIC OXIDE

Run no.	T, °K.	C_p	Run no.	T, °K	C_p	Run no.	T, °K.	C_p
1	71.3	2.580	25	224.4	9.378	49	201.1	8.344
2	73.7	2.710	26	237.9	9.211	50	204.5	8.503
3	75.8	2824	27	241.1	9.402	51	208.1	8.792
4	78.7	2.974	28	248.7	9.517	52	211.6	9.016
6	81.8	3.123	29	258.3	9.578	53	216.0	8.913
6	84.8	3.272	30	130.7	5.418	54	219.2	9.030
7	88.2	3437	31	133.7	5.531	55	228.8	9.415
8	91.7	3.574	32	138.1	5.704	56	246.0	9.336
9	95.2	3.739	33	153.8	6.389	57	261.2	9.589
10	99.5	3.972	34	157.2	6.564	58	280.6	9.852
11	108.5	4.416	35	163.0	6.802	59	284.9	9910
12	111.6	4.560	36	169.2	7.054	60	289.1	10 03
13	115.2	4.725	37	183.5	7 637	61	293.6	10 06
14	119.2	4.934	38	211.1	8.918	62	204.7	8 532
15	122.2	5.113	39	217.0	8.955	63	209.7	8 800
16	125.5	5.215	40	230.5	9.566	64	212.6	9 117
17	142.1	5.941	41	240.7	9.379	65	229.4	9.418
18	199.5	8.383	42	281.2	9.849	66	233.5	9.183
19	203.5	8.578	43	284.9	9.985	67	238.2	9.185
20	210.1	8.880	44	287.5	10.01	68	261.5	9.636
21	212.3	9.138	45	299.4	10.28	69	265.7	9.616
22	214.4	8.976	46	301.6	10.27	70	271.4	9.684
23	219.9	9.274	47	193.8	8.154			
24	221.3	9.215	48	197.6	8.239			

the magnetite, which they did not make, and part by a correction for loss of heat during the measurements.

A plot of the heat content–temperature curve shows that the heat capacity never becomes infinite, but reaches a maximum of 37.1 at 114.15°K The maximum is undoubtedly due to a change in the magnetic properties.

The first 46 points for cupric oxide, determined in October, 1926, were satisfactory below 200°K., but the measurements made above that temperature were inaccurate because the current through the resistance thermometer varied, due to the rapidly changing temperature of the room. In April of this year it was decided to repeat the measurements above this temperature. Fig. 3 shows all of the points between 180 and 270°K. taken at both times, with numbers corresponding to those in Table IV. It was surprising to find that two discontinuities in the heat capacity curve existed within a narrow range of temperature, and that the runs of the first series were not as inconsistent as was at first supposed. According to expectations the heat capacity in the neighborhood of 220°K. varied with the history of the sample, as will be seen by a comparison of the first and second series. The former was taken after cooling to liquid-air temperatures and heating step by step, and the latter after cooling to 190°K. and proceeding in the same manner, beginning with Run 47, and to 200°K., beginning with Run 62. It may be noted, however, that similar experiments[12] with mangano-manganic oxide and manganese dioxide showed the heat capacity of each of these substances to be independent of its history. Some preliminary measurements of the heat capacity of magnetite, made with an unsatisfactory calorimeter—later discarded—led to the conclusion that its history likewise did not affect this quantity. It will be noted that for manganous oxide, manganese dioxide, and magnetite the discontinuities of the heat capacity curves were very large in comparison with those of cupric oxide, and apparently took place with much greater ease and rapidity.

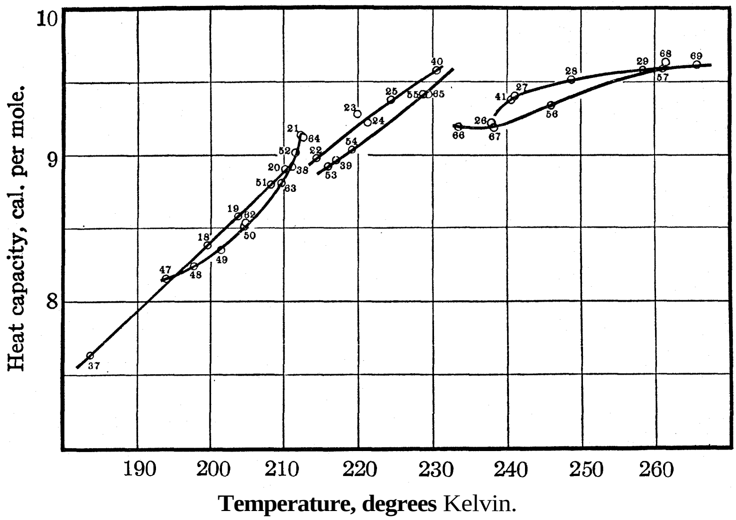


Fig. 3.—The molal heat capacity of CuO.

The Calculation of Entropy.—Obviously no sum of the theoretical equations so far devised, representing heat capacity as a function of the temperature, can be made to fit the data for ferrous oxide, magnetite and cupric oxide. However, if the upper and lower portions of the curve on the C_p–log T axes are connected by a curve representing the probable values of C_p, if no maximum were present, a combination of theoretical curves can be made to represent the interpolated curve with considerable accuracy and the entropy at some temperature below the interpolation can be calculated from the theoretical function.

In the following the Debye function is represented by $D(\beta\nu/T)$, and the Einstein function by $E(\beta\nu/T)$. For ferrous oxide the interpolation is rather large—from 89 to 282°K. The function

$$C_v = D\left(\frac{311}{T}\right) + E\left(\frac{387}{T}\right) + E\left(\frac{1265}{T}\right)$$

---

[12] Millar, This Journal, 50, 1875 (1928).

reproduces the lower portion of the experimental curve and the interpolation within 0.1% to 200°, and within 0.5% to 250° K. The total entropy at 25° is 12.7. Although this value exceeds the entropy of iron—6.71, calculated by Lewis, Gibson and Latimer[13]—more than the entropy of a monoxide usually exceeds that of the metal, yet it was found[12] that the entropy of manganous oxide was 14.92, whereas that of metallic manganese has been found by the above authors to be 7.3. The value for FeO, $S^\circ_{298} = 12.7$, is probably accurate within 2 units.

The interpolation under the peak in the curve representing the heat capacity of magnetite extends from 93 to 158°K. The function

$$C_v = 3D\left(\frac{346}{T}\right) + 4E\left(\frac{574}{T}\right)$$

represents the interpolation and the data above and below within 0.1% to room temperature. Calculation from the Debye function gives $S^\circ = 0.969$ at 44.7°K., and graphical integration above that temperature gives for Fe_3O_4, $S^\circ_{298} = 34.69$. Parks and Kelley[11] give 35.1, of which only 0.17 unit is due to their higher values of the heat capacity near room temperature. The agreement is excellent in view of the difficulty which they must have experienced in using the method of Lewis and Gibson[14] to obtain the entropy at 90°K., the lowest temperature at which they made a measurement, which is almost within the irregular portion of the curve. The present value is probably correct to 0.2 entropy unit.

An accurate calculation of the entropy of cuprous oxide is impossible, since the heat capacity is still over 8 at the lowest temperature. Furthermore, the four lowest points seem too high. The temperature scale may be in error at the lower end, although no uncertainty was anticipated before the calculation of the heat capacity, or these points may lie on the upper portion of an irregularity in the curve. However, the data can be well represented by the function $D(92/T) + E(235/T) + E(825/T)$, which represents the data within 0.3% up to room temperature, with the exception of the four lowest points. Calculation from the Debye function gives $S^\circ = 1.83$ at 25.1°K., and for Cu_2O, $S^\circ_{298} = 21.7 \pm 1.0$. It is hoped that the heat capacity of cuprous oxide at much lower temperatures will be obtained at a later date and thus permit a more satisfactory calculation of its entropy.

For cupric oxide the interpolation extends from 135 to 288°K. The function $D(443/T) + E(671/T) + E(1265/T)$ represents the data and the interpolation within 0.1% to 126° K., and within 0.5 to 224°K. The entropy calculated from the Debye function is 0.69 at 76.2°, and graphical integration over the remaining range gives for CuO, $S^\circ_{298} = 9.75 \pm 0.05$.

No reliable determinations of the heats of formation of the oxides of

---

[13] Lewis, Gibson, and Latimer, THIS JOURNAL, 44, 1008 (1922).

[14] Lewis and Gibson, *ibid.*, 39,2554 (1917).

iron have been made. Since such measurements will, it is hoped, be made in this Laboratory at a later date, calculations of the free energy of these substances will be deferred.

Although the data for the oxides of copper are of sufficient accuracy to permit calculations of their free energies, their consideration is most profitable in connection with the measurements of the e.m.f. of cells reported in the paper by Maier.[10]

Summary

The heat capacities of "ferrous oxide" and of cuprous and cupric oxide have been measured from 70 to 300°K., and of magnetite from 60 to 300°K.

Their entropies are:

	FeO	Fe_3O_4	Cu_2O	CuO
S°_{298}	12.7 ± 2.0	34.69 ± 0.2	21.7 ± 1.0	9.75 ± 0.05

BERKELEY, CALIFORNIA

NOTES

A Simple Apparatus for the Determination of Carbon Dioxide.—The following method has been worked out for the accurate determination of carbon dioxide in limestone. The originality, we believe, lies in the simplification of the apparatus and in the arrangement to minimize contamination with atmospheric carbon dioxide.

No special apparatus is required; two ordinary 1-liter Pyrex flasks, a small rubber balloon, two rubber stoppers and some large glass tubing are all that is necessary.

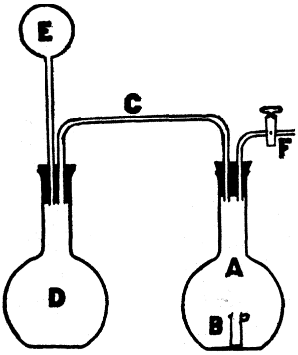


Fig. 1.

Chromic acid is used to liberate the carbon dioxide, and this is absorbed in a carefully standardized solution of barium hydroxide. The excess barium hydroxide is then titrated with standard hydrochloric acid, using phenolphthalein as indicator.

Procedure.—Set up the apparatus as shown in the figure and make sure that it is air tight. Weigh out 0.1000 g. of carbonate into B, place 100 cc. of a 1% aqueous solution of chromic anhydride in A and 50 cc. of water in D. Heat the contents of both A and D to boiling, remove both flames and add 25 cc. of a 0.2 N barium hydroxide solution to D. Carefully lower the bottle B containing the charge into A with a copper wire without letting the acid come in contact with the carbonate. Quickly stopper both A and D, which are thus connected by the tube C. Shake flask A to overturn B, place D in cold water and boil the contents of A. The balloon E serves as a safety valve, pressure regulator and pressure indicator. After boiling for about thirty minutes, remove the flame from beneath A and admit carbon dioxide-free air through F. The flask D should be now at about room temperature. Disconnect it and titrate the excess barium hydroxide with standard hydrochloric acid, using phenolphthalein as indicator.

The advantages of the method are that no train is necessary and the apparatus is cheap and easy to set up. It is likewise easy to clean. The results obtained are quite accurate. In the case of pure calcium carbonate 44.08 and 43.93 instead of 44.00% were obtained. With sodium carbonate the results were likewise accurate.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND
R. C. WILEY

RECEIVED JUNE 13, 1928
PUBLISHED JANUARY 8, 1929

Note on the Determination of the Activity of One Substance from that of Another by a Cell with a Liquid Junction.—In connection with work done in this Laboratory it was desired to know the activity coefficient of perchloric acid over a range of concentrations. On investigation of the literature, an article by Schuhmann[1] was found in which he states that the activity coefficient of perchloric acid is the same as that of hydrochloric acid of the same molality, at all concentrations up to 1.1 molal. His conclusions are based upon measurements of the cell H_2, $HCl(c)$, $HClO_4(c)$, H_2, since he obtains electromotive forces which are the same as those given by the Lewis and Sargent formula for this kind of liquid junction.

MacInnes and Yeh[2] have given a simple and reasonable derivation of this formula. When the cell operates, certain dilutions and concentrations will occur with respect to Cl^- and ClO_4^- in the composition gradient portion of the cell. (This composition gradient was of course set up by diffusion.) These effects are accompanied by the free-energy changes always involved in diluting or concentrating a substance. The "liquid potential" is the summation of these free energies, in joules per coulomb, when the cell operates reversibly. When the cell operates in a given direction, the relative speeds of Cl^- and ClO_4^- during current flow determine the extent to which the dilutions outweigh the concentrations, or the reverse, and this in turn determines the magnitude and sign of the "liquid potential," since dilution occurs with a decrease and concentration with an increase in free energy. MacInnes and Yeh derive the Lewis and Sargent formula, which involves the ion mobilities, by employing the ordinary equation for the free energy of dilution, assuming that the mobility and activity coefficient of each ion are constant over the entire gradient,

---

[1] Schuhmann, THIS JOURNAL, 46, 58 (1924).

[2] MacInnes and Yeh, *ibid.*, 43, 2563 (1921).

but not that the activity coefficients of all the ions are the same. They assume also a constant composition gradient. The assumption of a constant activity coefficient for a given ion is in accordance with experiment and with the well-known "principle of the ionic strength" of Lewis and Randall and the Debye-Hückel interionic attraction theory. They integrate the free energies of changes in concentration from a point beyond which no Cl^- ever enters to a point beyond which no ClO_4^- ever enters (using the above case as an example). The only reaction in the above cell not accounted for by these assumptions is the formation and disappearance of H^+ at the electrodes and its transport through the cell. If Schuhmann obtains the electromotive force given by the Lewis and Sargent formula, the formation and transport of H^+ must occur with no free-energy change. What these experiments seem to prove, then, is that the activity of H^+ in HCl solutions is the same as that of H^+ in $HClO_4$ solutions of the same molality, but not that the activity of Cl^- in aqueous HCl is the same as that of ClO_4^- in aqueous $HClO_4$ of the same molality. The experiments, therefore, do not prove that the mean activity of the ions, or the activity coefficient of the electrolyte, is the same for HCl and $HClO_4$ of the same molality. In fact, the use of mean activities is a mathematical device to avoid the use of individual ion activities, and is only exact for reactions which can be written in molecular form without arbitrary assignment of positive ions to negative ions, that is, reactions for which the product of the ion activities occurs in the equation connecting free energy with concentration. Practically all the cells used in activity determinations have been such as to involve the formation of the given compound from substances other than ions.

It is possible, of course, that Cl^- and ClO_4^-, because of the symmetrical electronic structure of both these ions, have the same activities in equimolal solutions of the two acids, up to 1.1 molal. Their mobilities are, in fact, nearly the same. It should be noted, however, that the individual ion activity of ClO_3^- is noticeably less than that of Cl^- in solutions of the same ionic strength, according to the table of Lewis and Randall. Other experiments of this type, or the determination of the activity of perchloric acid by freezing-point methods, might prove enlightening. Possibly the method could be used for the determination of individual ion activities. Meanwhile it is felt, in view of the above considerations, that the method used by Schuhmann is not evidence for equal mean activity coefficients in equimolal solutions of two electrolytes with a common ion.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF NEBRASKA

RALPH F. NIELSEN
HERMAN A. LIEBHAFSKY

RECEIVED SEPTEMBER 18, 1928
PUBLISHED JANUARY 8, 1929

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 28]

THE ACTION OF SULFURIC ACID IN THE PREPARATION OF CERTAIN ALKYL HALIDES

BY ROGERS MCCULLOUGH[1] AND FRANK CORTESE[2]

RECEIVED JULY 6, 1928 PUBLISHED JANUARY 8, 1929

During the course of our work, we had occasion to prepare alkyl halides of higher purity than ordinarily obtained. Michael and his co-workers[3] came to the conclusion that the purest halides were made by heating the corresponding alcohols with aqueous hydrobromic acid, according to Norris'[4] suggestion. They removed the small amount of unsaturated materials formed with potassium permanganate.

However, sulfuric acid is commonly used in the preparation of these halides.[5] While we have suspected for a long while the detrimental effects attending the use of this acid, we now have definite experimental proof that halides prepared by its aid tend to spoil more easily on keeping, developing colors and free halogen acid. We have shown that sulfuric acid splits out halogen acid, forming small quantities of olefins, which are then polymerized, the polymers adding on halogen acid to form unstable products and violet colors.

We have found that distilling the halide from a mixture containing sulfuric acid results in a decided increase in high-boiling products, particularly in the case of sensitive bromides, such as *iso*propyl, *sec.*-butyl and *iso*butyl. Except in the cases of *sec.*- and isobutyl bromides, all the bromides from ethyl to n-amyl contained very little high-boiling products when they were prepared by slowly distilling the alcohol from hydrobromic acid alone, according to Norris'[4] procedure. The amount of such products was greater for *iso*butyl than for *sec.*-butyl bromide. If the bromide obtained from the first distillation in the Norris method was returned to the acid flask and redistilled to improve the yield, as sometimes recommended, the additional time of heating resulted in an increase in polymers and other undesirable materials.

Allyl chloride and allyl bromide are commonly prepared by the aid of heat, and also by the use of sulfuric acid.[5] These halides, as ordinarily prepared, soon develop an extremely pungent odor, becoming lachrymators, and the bromide also develops a color. A simple cold process has been worked out for preparing these halides. The high-boiling residue

---

[1] Savage Fellow.

[2] Research Associate.

[3] Michael, Scharf and Voigt, THIS JOURNAL, 38, 653 (1916); Michael and Zeidler, Ann., 393, 81, 104 (1912); Michael and Leupold, ibid., 379,263,305 (1910).

[4] Norris, Am. Chem. J.,38,639 (1907); THIS JOURNAL, 38,1075 (1916).

[5] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1, 1 (1920).

is very small in this process. Furthermore, one distillation gives a product which remains for months water-white and maintains a perfectly clean odor, without any trace of sharpness, when stored in the dark in an ordinary bottle. The yields are poorer than those obtained in "Organic Syntheses,"[5] but our process is recommended when one wishes to sacrifice yield for quality, in making these halides for special work. The process also involves a minimum of apparatus and hardly any attention, although it requires a few days' time.

Experimental

Allyl Alcohol.--Solid potassium carbonate is added to Eastman practical allyl alcohol. The upper layer is removed and given the same treatment. After twenty-four hours it is filtered and used without distillation.

Allyl Chloride.—The alcohol is mixed with **8** times its volume of commercial hydrochloric acid (sp. gr., **1.19)** in a suitable well-corked bottle. After ten days the upper layer is washed once with **10%** sodium hydroxide and twice with **15%** sodium chloride, which minimizes emulsion formation. It is dried over calcium chloride and distilled. The yield of material boiling from 45–47° is from 55–65%. As an example: **204** cc. of crude alcohol with **1632** cc. of acid gave **144** g. of chloride.

If a small amount of halide is wanted in a hurry, the reaction is carried out in a sealed Pyrex bottle immersed in hot water **(60°).** Most of the yield, over 80%, is obtained in three hours.

Allyl Bromide.—A similar process is used. The alcohol: 48% acid ratio in cc. is **1:7.** The yields are 60–65%. Example: **410** cc. of crude alcohol with **2870** cc. of acid gave **478** g. of bromide, boiling from **69–73°.** The excess acid is recovered by distillation.

Allyl Iodide.—The alcohol: acid (sp. gr. **1.7)** ratio in cc. is **1:6.** The time is five days and the yield is 75–80%. Example: ten cc. of crude alcohol gave **10.3** cc. of iodide boiling from 99–103°.

Washing the Crude Halides.—In preparing *sec.*-butyl and *sec.*-amyl bromides by the Norris[4] method, the final products were extracted several times with concentrated sulfuric acid before washing. In some cases the halides were distilled from sulfuric acid. Invariably they turned pink on drying over calcium chloride. During distillation, hydrogen bromide was evolved, the material in the flask gradually assuming colors from pink through lavender to violet-red. The higher the temperature and the longer the contact with sulfuric acid, the worse were the colors and acid evolution. Repeated distillation tended to decrease these evils. We have found Norris' original recommendation of washing with concentrated hydrochloric acid a much better way of getting out the unchanged alcohol. By washing alkyl chlorides in this way and alkyl bromides with 48% hydrobromic acid, the troubles mentioned were reduced to a minimum.

In preparing pure bromides for the determination of their physical properties, to be reported by one of us in a forthcoming paper, the crude samples made by the Norris method were washed repeatedly with small portions of 48% hydrobromic acid until no volume change occurred. All alcohol and possibly some unsaturated products were thus removed. On returning the washings to the preparation flask and redistilling, a further quantity of bromide of a somewhat poorer quality was obtained. Bromides washed in this way gave no emulsion difficulties and on distillation gave very small light colored residues. Washing with sulfuric acid gave emulsions and highly colored residues with a disagreeable odor in the case of bromides easily attacked, e. g., *sec.*-butyl, particularly if the time of contact was long, even in the cold.

Careful fractionation of the products dried after the hydrobromic acid washing gave good yields of bromide of excellent purity. Constant boiling isopropyl bromide was obtained in 42% yields and *sec.*-butyl bromide, boiling over a 0.05" range, in 18% vielcls These pure bromides gave no test for unsaturated materials.

The Formation of Olefin and the Polymerizing Action of Sulfuric Acid.—Fifty cc. of secondary butyl bromide was made according to Norris' procedure and washed with hydrobromic acid. The colorless distillate had no odor of hydrogen bromide, but smelled somewhat unsaturated. The residue in the flask amounted to **3** cc. and had a deep violet color. On redistiliation, the first **3** cc. smelled highly unsaturated and used up 1.5 cc. of a 10% bromine solution in carbon tetrachloride. A fraction of a cc of the colored residue was diluted with chloroform until the color just faded. On adding 1 cc. of acetic anhydride and then one small drop of concentrated sulfuric acid (Burchard test)[6] a faint violet color appearing in one-half minute, developed to a distinct color in a few minutes. A fraction of a cc. was diluted with chloroform to a light pink. Thr Burchard test gave an immediate blue-violet tint and increased depth of color. In ten minutes it was fairly deep greenish violet. After two days the color had faded badly and a ring of purplish red resin had formed around the surface of the liquid. This substantiates the theory proposed by one of us (to be published later) that the Burchard test reagents and similar reagents cause polymerization to form colloidal particles. The color effects are then understood by applying Wo. Ostwald's colloidal theory of color.[7]

In making secondary butyl bromide, by heating the alcohol with acid in a sealed tube at 60°, the amount of unsaturation found was 1%, calculated as dibutene. Five cc. of secondary butyl bromide containing 2% of *sec.*-butyl alcohol was shaken with 5 cc. of concentrated sulfuric acid at room temperature. The volume change indicated that the alcohol had been extracted but even after a few minutes' shaking a small amount of emulsion had formed. After standing for two hours the attack on the bromide was pronounced and standing overnight gave a viscous, dark brown mixture. The use of 70% sulfuric acid reduced the trouble but a small amount of viscous oil also was formed after standing overnight.

Isopropyl, *sec.*-butyl and *sec.*-amyl bromides, especially after sulfuric acid treatment, on drying with calcium chloride assume delicate light blues, pinks, violets and lavenders and become opalescent, the degree of opalescence depending on the depth of the shade of red. Experiment showed that these effects are chargeable to the sulfuric acid treatment.

Three cc. of pure isopropyl bromide was added to 2 cc. of chloroform. One cc. of acetic anhydride and one drop of concentrated sulfuric acid were then added. In forty-eight hours a dark violet color resulted.

One drop of a 2,4-hexadiene dimer was dissolved in 5 cc. of chloroform. One drop of concentrated hydrochloric acid was added and the whole was shaken. Within half a minute the solution had assumed the typical pink color developed by ordinary *sec.*-butyl bromide on standing over calcium chloride, showing that the colors also could be produced by the action of the halogen acid on the unsaturated polymers.

Not all bromides are noticeably attacked by sulfuric acid. n-Butyl bromide seems to be the most stable of all those studied by us. When washed with either sulfuric or hydrobromic acid, it gave an equally good product. The residues from the distillations show only a faint color. Ethyl and n-propyl bromides are more sensitive. In fact, they are sufficiently sensitive for us to recommend only the hydrobromic acid treatment. Isobutyl bromide is quite sensitive and the secondary bromides are so easily attacked that we feel it is very undesirable to use sulfuric acid when pure products are desired.

---

[6] Burchard, Chem. Zentr., I, 25 (1890).

[7] Wo. Ostwald, *Kolloidchem. Beihefte,* 2, 409–488 (1911); Chem. Zentr., II, 1407 (1911).

Summary

1. Convenient methods for making allyl halides are described. Allyl bromide and allyl chloride made in this way do not develop objectionable odors and colors on standing.

2. Sulfuric acid is to be condemned in the preparation of pure alkyl halides.

3. In the preparation of pure alkyl halides, even by the Norris method, a small amount of unsaturated materials is formed.

4. Sulfuric acid not only polymerizes these materials but attacks sensitive halides to form more unsaturated materials.

5. The colors of decomposing halides are caused by the action of sulfuric acid and halogen acid on the unsaturated materials.

6. The Norris procedure gives the purest products.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. I. OXIDATION OF CROTONIC AND ISOCROTONIC ACIDS, OF THE LACTONE OF 3-HYDROXY-ISOCROTONIC ACID AND OF MALEIC ANHYDRIDE

BY GÉZA BRAUN[1]

RECEIVED JULY 13, 1928 PUBLISHED JANUARY 8, 1929

I. Oxidation of Crotonic and Isocrotonic Acids

According to the van't Hoff-Wislicenus theory there are two isomeric 2-methylacrylic acids, the cis and trans. In the opinion of Auwers[2] the cis form represents isocrotonic and the trans form crotonic acid. Since this pair of acids has active double bonds and has been thoroughly studied from the point of view of cis-trans isomerism, these acids are very well suited for the study of the addition of hydroxyl groups.

Several different methods for the oxidation of crotonic acid are reported in the literature. MelikoE[3] oxidized it with hypochlorous acid and prepared a dihydroxybutyric acid (m. p. 80°) through the intermediate formation of 2-methylglycidic acid. Fittig and Kochs[4] used barium permanganate, Glatffeld and Woodruff[6] potassium chlorate; in both cases the identical dihydroxybutyric acid, m. p. 74–75", was obtained.

The pure, crystallizable isocrotonic acid had not previously been used for oxidation. Melikoff and Petrenko-Kritschenko[6] succeeded in pre-

---

[1] International Research Fellow in Organic Chemistry from Hungary.

[2] Auwers and Wissebach, Ber., 56, 715 (1923).

[3] Melikoff, Ann., 234, 197 (1886).

[4] Fittig and Kochs, *ibid.*, 268, 7 (1892).

[5] Glattfeld and Woodruff, THIS JOURNAL, 49, 2309 (1927).

[6] Melikoff and Petrenko-Kritschenko, Ann., 266, 359 (1891).

paring crystallized dihydroxybutyric acid (m. p. 45°) by the oxidation of Geuther's[7] crude isocrotonic acid, which contained crotonic and tetrolic acids.[8] Fittig and Kochs[4] and later Morrell and Bellars[9] failed to get crystallized products with barium permanganate. They obtained only sirups which did not crystallize or which occasionally contained a few crystals.

The whole situation was rather confused in many respects. The yields of pure dihydroxybutyric acids were cut down by side reactions and isomerizations to such an extent that they were not higher than 20–25%. It was therefore necessary to work out new methods which would show the relation between the crotonic acids and the dihydroxybutyric acids and which would give sufficiently high yields for the study of the addition of hydroxyl groups.

This paper is a report of (A) perbenzoic acid oxidations of crotonic and isocrotonic acids for the *trans* addition of the hydroxyl groups. The method gave a yield of 63% of dihydroxybutyric acids from both crotonic and isocrotonic acids. (B) Chlorate oxidations of these two acids for the cis addition of the hydroxyl groups. The yields were as high as 82% in both cases.

(A) Oxidations by Means of Perbenzoic Acid

(a) Oxidation of Crotonic Acid (m. p. 72°).—In one of his recent papers, Böeseken[10] states that crotonic acid cannot be oxidized with perbenzoic acid. Although the reduction of the per-acid is so very slow as to be easily overlooked, as a matter of fact the oxidation of crotonic acid proceeds very well in both aqueous and non-aqueous solutions.

Among the various methods for the oxidation in the presence of water, Bergmann's[11] method was found to be the best: crotonic and perbenzoic acids were dissolved in chloroform and this solution was shaken with much water. The oxidation takes place in the chloroform phase and the water removes the oxidized product immediately. The yield was about 88% of a viscous sirup which yielded from ethyl acetate 63–64% of crystals, m. p. 81.5°. This product was a dihydroxybutyric acid. Its melting point did not change when the substance was mixed with the acid obtained by the oxidation of isocrotonic acid with silver chlorate (see later). The molecular weight, according to titration, was 121. This corresponds to a formula $C_4H_8O_4$.

The mother liquor from the crystals melting at 81.5° was a non-crystallizable sirup. According to titration it was a mixture of the dihydroxy-

[7] Geuther, Z. *Chem.*, 242 (1871).

[8] Michael and Schulthess, J. *prakt. Chem.*, [2] 46, 248 (1891).

[9] Morrell and Bellars, J. *Chem. Soc.*, 85,350 (1904).

[10] Boeseken, Rec. trav. *chim.*, 45, 838 (1926).

[11] Bergmann and Schotte, *Ber.*, 54, 440, 1564 (1921).

butyric acid and perhaps its lactide. Probably both of the theoretically possible *dl*-1,2-dihydroxybutyric acids were present. As there is at present no known method for the separation of these acids or their derivatives, the sirup was not further investigated.

It is an interesting fact that crotonic acid even in pure water solution can be oxidized with perbenzoic acid. However, the yields were not higher than 30–40% of crystallized product, m. p. 81.5°, when either concentrated or diluted solutions of the per-acid were used.

(b) Oxidation of Isocrotonic Acid (m. p. **15.5°**).—The oxidation was carried out under conditions which had been found to be most favorable in the treatment of crotonic acid. The yield of crude product was 90% of the theoretical; that of crystalline product, m. p. 74–75', was 62–63% of the theoretical. A mixture of this acid (75") with the acid obtained by the oxidation of crotonic acid with chlorate (75°) showed no depression of the melting point.

The oxidation of isocrotonic acid in aqueous solution was more successful than that of crotonic acid but very slow. The yield of dihydroxybutyric acid, m. p. 74°, was about 65% of the theoretical.

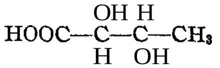
The oxidation of both crotonic and isocrotonic acids in non-aqueous solution is now in progress.

Discussion of the Results

The perbenzoic acid oxidation of crotonic acid gave a dihydroxybutyric acid, m. p. 81.5°, which is identical with the acid obtained from isocrotonic acid by oxidation with chlorate and which must be the same as Melikoff's acid, m. p. 80°.

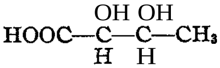
The perbenzoic acid oxidation of isocrotonic acid gave a dihydroxybutyric acid, m. p. 74–75'; this is the same acid that was obtained from crotonic acid with chlorates and permanganate.[5]

According to theory there are two *dl*-1,2-dihydroxybutyric acids. It is suggested that the prefixes *threo* and erythro be attached to the names of these substances to distinguish them and to show their relations to the well known threonic and erythronic acids



$$\mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}CH_3}$$

dl-threo-1,2-Dihydroxybutyric acid



$$\mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_3}$$

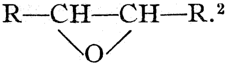
dl-erythro-1,2-Dihydroxybutyric acid

One of these dihydroxybutyric acids melts at 74–75", the other at 81.5°; but which of these is the threo form and which the erythro form cannot be decided so satisfactorily as in the case of the tartaric acids, where one form is internally compensated and the other is not. However, if the configuration of the crotonic acids is assumed[2,12] and advantage is taken of the experience of other workers in regard to the manner of addition of hydroxyl

---

[12] For objection see Kuhn and Ebel, *Ber.*, 58, 925 (1925).

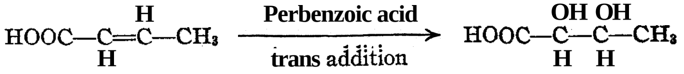
groups at a double bond, it is possible to assign configurations to the two acids in question with a considerable degree of assurance.

It has been shown[11,13] many times that in the oxidation by perbenzoic acid the first step is the formation of an ethylene oxide ring,  $R{-}\underset{\diagdown O \diagup}{CH{-}CH}{-}R$.[2] In the presence of water this ring opens and the compound is converted into the 1,2-glycol. In both steps there is a possibility of formation of both cis or trans compounds.

The oxidation of crotonic and isocrotonic acids with perbenzoic acid gave the dihydroxybutyric acids, isomeric with those obtained in the chlorate oxidations; that is, crotonic acid with perbenzoic acid yielded the *dl*-1,2-dihydroxybutyric acid, m. p. 81.5°, and with silver chlorate the *dl*-1,2-dihydroxybutyric acid, m. p. 75°. Assuming that the configurations ordinarily assigned to maleic and fumaric acids are correct, then it may be said that no case of inversion has ever been observed in a chlorate oxidation. On later pages of this paper will be found evidence supporting this statement. Hence the acid obtained by oxidation with perbenzoic acid is not the same as the acid obtained by chlorate oxidation, and therefore the oxidation with perbenzoic acid must involve a single inversion—either trans formation or trans splitting of the ethylene oxide ring.

There is no work reported in the literature to show whether the direct formation of the ring by oxidation of a double bond is cis or trans; but the trans splitting of the ring in the presence of water seems very probable from the work of Böeseken.[14] According to Kuhn and Ebel,[12] this trans splitting of the oxide rings is a general occurrence and in one case it was definitely proved: the hydrolysis of the internally compensated *cis*-ethylene-oxide-dicarboxylic acid yielded exclusively racemic tartaric acid. The proof in this case is based on the optical properties of both starting and end products. It seems, therefore, to be free from objections. So it seems probable that in the perbenzoic acid oxidations there is a *cis* formation of the oxide ring and then, in the presence of water, a trans splitting of the ring; this means a trans addition of the hydroxyl groups to the double bond.

Now if it be assumed that the oxidations of crotonic and isocrotonic acids by perbenzoic acid run in the same way as in the cases cited, then the two reactions may be written as follows:



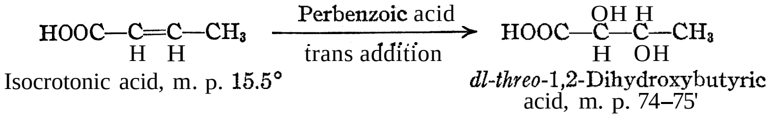
$$HOOC{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3 \xrightarrow[\text{trans addition}]{\text{Perbenzoic acid}} HOOC{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}CH_3$$

Crotonic acid, m. p. 72° *dl-erythro*-1,2-Dihydroxybutyric acid, m. p. 81.5°

---

[13] Prileschajew, *Ber.*, 42, 4811 (1909).

[14] Böeseken, *ibid.*, 56, 2409 (1923).



$$HOOC-\underset{H}{C}=\underset{H}{C}-CH_3 \xrightarrow[\text{trans addition}]{\text{Perbenzoic acid}} HOOC-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$$

Isocrotonic acid, m. p. 15.5°

dl-threo-1,2-Dihydroxybutyric acid, m. p. 74–75'

This means that the acid of m. p. 74–75' is the *threo* form and the acid of m. p. 81.5' is the *erythro* form.

(B) Oxidation of Crotonic and Isocrotonic Acids with Barium and Silver Chlorates with Osmic Acid as a Catalyst

(a) Oxidation of Crotonic Acid with Barium Chlorate.—The oxidation of crotonic acid by means of potassium chlorate with osmic acid as catalyst was recently carried out by Glattfeld and Woodruff.[5,15] A more careful study of this oxidation showed that there was a strong decrease in the initial acidity. This must be due to side reactions, since simple addition of hydroxyl groups to crotonic acid would not change its total acidity, and lactone formation cannot be assumed in this case. In order to clarify the mechanism of this reaction barium chlorate was used instead of potassium chlorate because it may be removed quantitatively from the reaction mixture.

Even under the most favorable conditions used—when the oxidation was carried out in dilute solution at room temperature—there was found a decrease of about 24% in the total acidity after the oxidation was complete. After all of the inorganic matter had been removed, there was found to be a large amount of organically bound chlorine in the solution. This chlorine proved to be present as a chlorohydroxybutyric acid, the formation of which may be explained only by the addition of the *free* hypochlorous acid to the crotonic acid. This is also the reason for the decrease in the acidity; the decrease in acidity is directly proportional to the absorption of hypochlorous acid.[16]

In the most successful of the oxidation experiments carried out, about 20% of the crotonic acid was chlorinated, so that in the reaction mixture in these experiments there were present the dihydroxybutyric acid and chlorohydroxybutyric acid as chief products. The separation of the two acids was very simple: the water was completely removed by distillation at reduced pressure and the dihydroxybutyric acid was separated by crystallization from ethyl acetate as completely as possible. The mother liquor contained the chlorohydroxybutyric acid. The yield of dihydroxybutyric acid (m. p. 74°) was 38% of the theoretical.

The mother liquor was shaken two or three times with water in order to remove the rest of the dihydroxybutyric acid; the ethyl acetate was removed by distillation, leaving the crude chlorohydroxybutyric acid as a

---

[15] Medwedew and Alexejewa, "Papers on Pure Appl. Chem. Karpow-Inst.," Moskau, 1927, *Chem. Zentr.*, *[2]*1012 (1927).

[16] Formation of lactides, of course, also decreases the acidity.

sirup which was identified by analysis but which could not be rendered crystalline. The crystallized acid (m. p. 76°) could be prepared only from the crystallized zinc salt. That this acid was a chlorohydroxybutyric acid was shown by analysis for chlorine and by titration. On account of the small quantity its structure could not be determined.

The addition of hypochlorous acid to crotonic acid in the oxidation experiments with chlorates is then a fact. This chlorination could not be avoided although the oxidation was carried out under various conditions. It was a little lower when the barium chlorate was added gradually during the oxidation and considerably lower (about 3%) when the neutral barium crotonate was oxidized. But the oxidation of barium crotonate is not a practicable method because it is extremely slow: after one year about 30% of the crotonic acid was still present under circumstances in which the oxidation in acid solution was complete in ten days. That the chlorate oxidations do not proceed in neutral solution was recently observed also by Milas.[17]

(b) Oxidation of Crotonic Acid with Potassium **Chlorate.**—The results of the oxidations with potassium chlorate were exactly the same as those with barium chlorate. A potassium-acid double salt was separated in this case as an intermediate product. According to analysis it had the approximate formula $C_4H_7O_4K \cdot C_4H_8O_4$. The product is very soluble in water and hot absolute alcohol, from which it may be recrystallized; it is insoluble in ethyl acetate. For identification it was dissolved in water and the calculated amount of sulfuric acid was added. The dihydroxybutyric acid (m. p. 74°) was obtained with 80% yield. The product was not further investigated.

(c) Oxidation of Crotonic Acid with Silver **Chlorate.**—We have just seen that oxidation with barium and potassium chlorates does not proceed without the simultaneous addition of hypochlorous acid, whether the free crotonic acid or barium crotonate is used. When silver chlorate was used, however, hypochlorous acid addition was reduced to a minimum. This advantage of the silver chlorate is due to the following facts. The silver chloride precipitates as soon as formed; the silver hypochlorite is a very unstable compound and decomposes immediately according to the equation $3AgOCl = AgClO_3 + 2AgCl$. The addition of the hypochlorous acid to the double bonds is therefore greatly reduced.

Two sets of experiments were carried out with silver chlorate: in one set the necessary amount of chlorate (30% excess over the theoretical) was added in one operation at the beginning of the oxidation; in the other set the chlorate was added gradually in order to keep its concentration during the oxidation as low as possible.

In the first set the yield of dihydroxybutyric acid (m. p. 74°) was about

---

[17] Milas, This Journal, 49, 2010 (1927).

60% of the theoretical; about 5% of the crotonic acid was chlorinated under these conditions. The silver salt of the dihydroxybutyric acid (m. p. 74°) was separated as an intermediate product. This silver salt crystallized out when the purified water solution of the dihydroxy acid was concentrated at reduced pressure and could be isolated with absolute alcohol. (One should handle the alcoholic silver precipitates in the presence of chlorate very carefully.)

When the silver chlorate was gradually added in small portions (the second set), practically no chlorination occurred. The osmic acid itself was used as indicator for the course of the oxidation: when the silver chlorate was used up, the color of the solution became brown due to the formation of the lower oxides of osmium. The color disappeared in a short time (even at 0°) after addition of more chlorate. The yield of oxidized product was about 92% and that of crystallized product (m. p. 74°) 70% when the oxidation was carried out at room temperature. When the oxidation was carried out at 0°, the yield of desired product was almost quantitative. Only a small quantity of oxalic and volatile acids was formed. The yield of the crystallized dihydroxybutyric acid (m. p. 74°) was as high as 82% of the theoretical. Investigation of the non-crystallizable sirup—which contained a great deal of dihydroxybutyric acid—is now in progress,

A complete summary of the oxidations carried out with crotonic acid' in 2% aqueous solution is given in Table I.

TABLE I

SUMMARY OF OXIDATIONS

25% excess of chlorate used. Room temperature in first five, 0° in last

Chlorate of	Added	OsO_4 per 100 g. of crotonic acid, g.	Dur. of oxid., weeks	Decr. in init. acidity, %	Crotonic acid chlor., %	Yield of oxid. prod., %	Yield of di-OH-butyric acid (75°) %	Other crystalline products
Ba	At once	0.125	1	24	20	79	38	$C_4H_7O_3Cl$ (m. p. 76°)
Ba	Gradually	.25	4	24	20	89	48	$C_4H_7O_3Cl$ (m. p. 76°)
K	Gradually	.25	4	24	20		.	$C_4H_7O_4K$, $C_4H_8O_4$
Ag	At once	.25	1	7	5	90	60	$C_4H_7O_4Ag$
Ag	Gradually	.25	4	3	1.5	92	70	....
Ag	Gradually	.5	4	0	1.5	96	82	....

(d) Oxidation of Isocrotonic Acid (m. p. 15°) with Silver Chlorate.—The oxidation was carried out by the gradual addition of silver chlorate at 0° in exactly the same manner as with crotonic acid. The yield of oxidized product was 97%; this gave 82% of the theoretically possible amount of crystalline product (m. p. 81.5'). The mixture of this acid with the acid obtained by the oxidation of crotonic acid with perbenzoic acid showed no depression of the melting point.

II. Oxidation of the Lactone of the 3-Hydroxy-isocrotonic Acid with Silver and Barium Chlorates

The lactone was prepared by Lespieau[18] and oxidized with alkali chlorates by Glattfeld and Cohen[19] with good yield. The oxidation was repeated with silver and barium chlorates at room temperature. The yield of erythronic lactone (m. p. 89–90°) in the silver chlorate oxidations was as high as 75% of the theoretical; in the barium chlorate oxidation it was a little lower, 64% of the theoretical. The recrystallized erythronic lactone melted at 92°. For identification it was oxidized with dilute nitric acid according to Anderson[20] and yielded, except for a small amount of oxalic acid, exclusively mesotartaric acid.

In no case was there found any chlorinated compound; the lactone has a very inactive double bond and shows great resistance to the addition of hypochlorous acid.

III. Oxidation of Maleic Anhydride

The oxidation of maleic anhydride and of maleic and fumaric acids with perbenzoic acid was attempted under various conditions but in no case did oxidation occur. This agrees with the observation of Böeseken[10] and Kuhn.[12]

The oxidation of maleic anhydride with barium chlorate in dilute aqueous solution was as successful as that of maleic and fumaric acids described by Milas and Terry.[21] A great difference between the barium and silver chlorate oxidations was observed, while the oxidation with barium chlorate was almost quantitative; the oxidation with silver chlorate under the same conditions gave only a 70% yield of mesotartaric acid. The ratio of the yields with the two chlorates in question, when maleic and fumaric acids were oxidized, was found to be the same. Silver chlorate in these cases is therefore not suitable for the oxidations.

No chlorination was observed in the chlorate oxidations; maleic anhydride (as well as maleic acid in water solution) has an inactive double bond and adds hypochlorous acid only slowly in acid solution.

Discussion of the Results

Hofmann first used activated chlorates for the oxidation of unsaturated compounds.[22] He states that the action of chlorates on ethylene double bonds in the presence of osmic acid in neutral solution, in solutions slightly

---

[18] Lespieau, Bull. *soc. chim.*, [3] 33, 460 (1905); Glattfeld and Leavell, unpublished results.

[19] Glattfeld and Cohen, unpublished results.

[20] Anderson, *Am. Chem.* J., 42, 429 (1909).

[21] Milas and Terry, THIS JOURNAL, 47, 1412 (1925).

[22] Hofmann, Ehrhart and Schneider, Ber., 46, 1657 (1914).

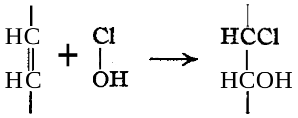
alkaline with bicarbonate or in weakly acid solutions, is exactly the same as that of potassium permanganate, and the reduction of chlorates to chlorides does not pass through the lower oxides of chlorine; the potassium chlorate is reduced directly to potassium chloride. So Hofmann writes the equation for the reaction as follows: $2OsO_4 = Os_2O_5 + 3O$ and $Os_2O_5 + KClO_3 = 2OsO_4 + KCl$.

Milas and Terry [21] recently investigated the oxidation of fumaric and maleic acids by alkali chlorates; they state that the principal reduction products of chlorate in the reaction are chlorite and chloride, principally the latter. The presence of traces of hypochlorous acid and free chlorine was shown by qualitative tests.

Now, the work on the oxidation of crotonic acid by chlorates reported in the present paper shows that: (1) when the crotonic acid is oxidized with barium or potassium chlorate—whether the chlorate is added at the beginning in one operation or added gradually during the oxidation—about 20% of the crotonic acid is chlorinated by the addition of hypochlorous acid; (2) if barium crotonate is oxidized in *neutral* solution, about 3% of the crotonic acid is chlorinated; (3) even in the presence of silver chlorate there occurs 5% chlorination, when the concentration of the silver chlorate is great; and (4) practically no chlorination occurs if the concentration of the silver chlorate is kept as low as possible.

As mentioned before, the addition of hypochlorous acid is an established fact. For the source of the hypochlorous acid which is added there are two possibilities.

1. "Status nascens" Addition.—According to the law of mass action, free chloric acid must be present when a metal chlorate is added to a water solution of an acid: $RCH{=}CHCOOH + MeClO_3 \rightleftarrows RCH{=}CHCOOMe + HClO_3$. The chloric acid will be reduced by the catalytic action of the osmic acid: $HClO_3 \longrightarrow HClO_2 \longrightarrow HClO$. When the reduction has proceeded to the hypochlorous acid stage, two reactions occur simultaneously: one part of the hypochlorous acid is further reduced to hydrogen chloride and another part adds "status nascens" to the double bond



$$\begin{array}{c} | \\ HC \\ \| \\ HC \\ | \end{array} + \begin{array}{c} Cl \\ | \\ OH \end{array} \longrightarrow \begin{array}{c} | \\ HCCl \\ | \\ HCOH \\ | \end{array}$$

If the concentration of the chloric acid, and therefore of the hypochlorous acid, is very low, then there is sufficient osmic acid present to reduce the hypochlorous acid almost completely, and the addition of the hypochlorous acid to the double bond will occur practically not at all. This may be the explanation of the fact that there was very little chlorination when the oxidation of crotonic acids was carried out with silver chlorate and when the concentration of the chlorate was kept as low as possible, while 5% chlorination occurred when the silver chlorate was used in excess.

2. "Secondary" Addition.—After a certain amount of chloric acid has been reduced to hydrogen chloride, these compounds react with the formation of chlorine: $HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O \longrightarrow 3HCl + 3HClO$, and the hypochlorous acid thus formed adds to the double bond.

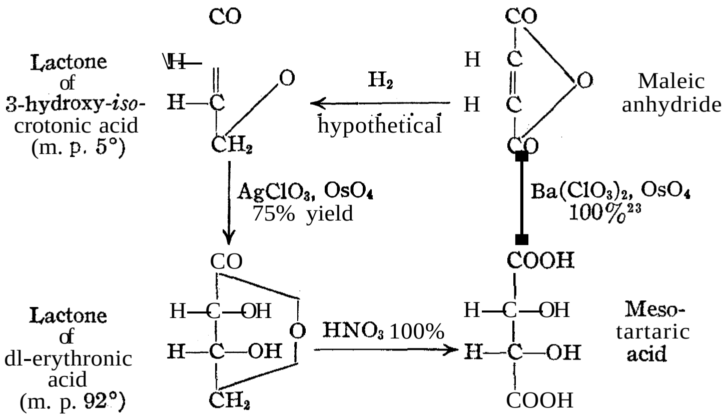
The chlorination of the neutral barium crotonate and chlorination in the presence of silver chlorate point to the "status nascens" source of the hypochlorous acid; in these cases the concentration of the hydrogen chloride is very low and the "secondary" source is not probable. However, if chlorates which give soluble chlorides, such as barium, potassium chlorate, etc., are used, then it is very probable that the hypochlorous acid added comes from both sources, for only a slight difference was observed when the crotonic acid was oxidized by the addition of barium chlorate in one operation at the beginning or by gradual addition of the barium chlorate throughout the oxidation. If the "status nascens" source of the hypochlorous acid were the only source, then in the latter case there would have been much less chlorination, just as in the case of silver chlorate oxidations; but the results of the oxidation with barium chlorate under the two sets of conditions were almost identical, showing that hypochlorous acid was produced by both methods.

In conclusion, it seems to be very probable that in every case the reduction of chlorates passes through the lower oxides of chlorine and some of the hypochlorous acid added is generated by the "status nascens" process; and not only in strong acid solution, as Hofmann stated, but even in weakly acid solution, there is a reaction. between the chloric and hydrochloric acids with the formation of hypochlorous acid.

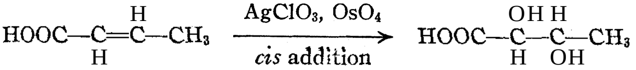
The mechanism of the catalytic action of osmic acid will not be treated at the present time.

The Manner of Addition of Hydroxyl Groups to Double Bonds in Chlorate Oxidations

It has been shown many times in the literature that in the case of chlorate oxidations with osmic acid—when an unsaturated compound was oxidized—just as in case of potassium permanganate oxidations, there is a cis addition of the hydroxyl groups. Milas and Terry[21] improved Hofmann's method and obtained an almost quantitative yield when fumaric acid was oxidized to *racemic* tartaric acid and maleic to mesotartaric acid, and, recently, Glattfeld and Cohen oxidized "maleic"—the lactone of 3-hydroxy-isocrotonic acid, to dl-erythronic lactone. All of the above oxidations were now repeated but under the same conditions that were used with crotonic acid; the results of these experiments are given below and show that the addition of the hydroxyl groups is *cis*.



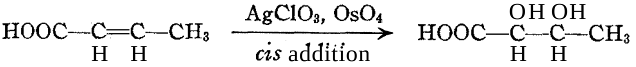
The silver chlorate method of oxidation of crotonic acid yielded *dl*-1,2-dihydroxybutyric acid (m. p. 74–75') and isocrotonic acid yielded by the same method *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°). Now if it is assumed that the oxidations of crotonic and *iso*crotonic acids proceed in the same way as in the former cases, these reactions may be indicated as follows



$$\mathrm{HOOC{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3} \xrightarrow[\textit{cis}\ \text{addition}]{\mathrm{AgClO_3,\ OsO_4}} \mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}CH_3}$$

Zrotonic acid (m. p. 72°) *dl-threo*-1,2-Dihydroxybutyric acid (m. p. 74–75')

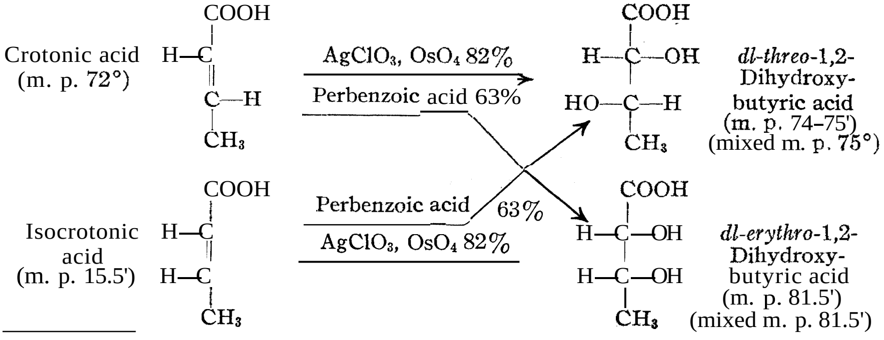
and



$$\mathrm{HOOC{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3} \xrightarrow[\textit{cis}\ \text{addition}]{\mathrm{AgClO_3,\ OsO_4}} \mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_3}$$

Isocrotonic acid (m. p. 15.5°) . *dl-erythro*-1,2-Dihydroxybutyric acid (m. p. 81.5')

These results are in perfect harmony with those obtained in the perbenzoic acid oxidations, which makes the configurations assigned to the



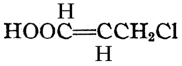
---

[23] By 100% in yield is meant that the isomer indicated was formed exclusively with very high yield. (For instance, in the oxidation of maleic anhydride with barium chlorate there was obtained exclusively mesotartaric acid with an actual yield of 91% and no trace of racemic tartaric acid.)

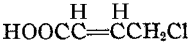
dihydroxybutyric acids above still more probable. A complete summary of all the oxidations carried out with chlorates and perbenzoic acid is given above.

A better means of determining these configurations would be the oxidation of the two acids to the corresponding tartaric acids, but this unfortunately appears to be impossible. There does, however, seem to be a possibility of obtaining better evidence by an indirect method. If the two 3-chloro acids[24] were prepared, their relation to crotonic and isocrotonic

3-Chloro-crotonic acid



$\mathrm{HOO}\overset{\mathrm{H}}{\mathrm{C}}{=}\underset{\mathrm{H}}{\mathrm{C}}\mathrm{CH_2Cl}$



$\mathrm{HOOC}\overset{\mathrm{H}}{\mathrm{C}}{=}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{CH_2Cl}$

3-Chloro-isocrotonic acid

acids could be demonstrated by reduction with sodium amalgam. The oxidation of these chloro acids should yield a *threo* and an *erythro* 3-chloro-dihydroxybutyric acid. Hydrolysis of these two acids should yield threonic and erythronic acids; oxidation should give mesotartaric and racemic acids; reduction should yield the two dihydroxybutyric acids. Work on these reactions is now in progress.

Experimental Part

Materials

Crotonic Acid.—The commercial product may be used without further purification. The best method for its preparation has been recently described by Auwers.[25]

Isocrotonic Acid.—This was prepared from the commercial product and from Geuther's crude isocrotonic acid according to the method of Wislicenus.[26]

Lactone of 3-Hydroxy-isocrotonic Acid.—The lactone is a by-product in the preparation of *dl*-2,3-dihydroxybutyric acid and may be prepared according to Glatffeld's method[18] with good yield. The crude product was recrystallized twice from one and a half parts of absolute ether, cooled in ice and salt, and the crystals were dried at 0° over phosphoric anhydride in a vacuum desiccator. The melting point of the product was 5.0 to 5.3° (thermometer in the substance).

Perbenzoic Acid.—This was prepared according to Baeyer and Villiger,[27] except that chloroform was used instead of ether as a more suitable solvent for the benzoyl-peroxide. One has to be very sure that all of the materials used in the preparation of the peracid are pure because the oxidations require a long time and an impure peracid decomposes before the oxidations are complete.

Silver Chlorate.—The best method for the preparation of this substance consists in the solution of silver oxide in a slight excess of 10% chloric acid[28] at 30°. The filtrate is concentrated at reduced pressure and the concentrated solution of silver chlorate cooled in ice. The chlorate of silver is just as stable a compound as the chlorates of alkali metals.

The precipitate obtained in the silver chlorate oxidations is almost pure silver

---

[24] The trans compound is known; Lespieau, *Bull. soc. chim.*, [3] 33, 466 (1905); Auwers and Wissebach, Ber., 56, 732 (1923).

[25] Auwers, Ann., 432, 46 (1923).

[26] Wislicenus; see Beilstein's "Handbuch der organische Chemie."

[27] Baeyer and Villiger, Ber., 33, 1575 (1900).

[28] Vauquelin, Ann. *Chim.*, 95, 124 (1915).

chloride. In order to purify it one has to wash it with warm dilute hydrochloric acid and then with water so as to remove oxalic acid and other impurities. It is dried as completely as possible by suction filtration. The pure, moist silver chloride thus obtained (containing about 6–8% of moisture) is suspended in five times its weight of water and, while the mixture is being violently stirred, a 50% excess of zinc dust is rapidly added. The solution becomes hot; the stirring is continued until the solution has cooled to room temperature and then the excess of the zinc is dissolved with 20% sulfuric acid without interrupting the stirring. The gray-brown precipitate is separated by filtration and washed thoroughly. The precipitate still contains a considerable amount of silver chloride and the operation must be repeated with a small amount of zinc dust in order to obtain pure silver, which may be used in the making of silver chlorate. The yields are almost quantitative.

Control of the Oxidations

The best control of the oxidations is the quantitative determination of the unsaturated compounds in the reaction mixture. No general method for this purpose has been published in the literature, as the behavior of unsaturated compounds differs very widely according to the reagents used in the determinations. Bromine water seems to be the most suitable reagent. When this reagent is used the acidity of the reaction mixture is very important; one group of unsaturated compounds—those having *active* double bonds—may be brominated quantitatively even in the presence of mineral acids, while another group—those having *inactive* double bonds—can be brominated only in neutral solution.

In order to find a reliable method for the control of the oxidations, many experiments were carried out for the determination of double bonds of unsaturated acids.

In every case a stock solution was made of such concentration that 25 cc. contained about 0.1 g. of unsaturated substance. In using Winkler's method,[29] there was added to 25 cc. of the stock solution 2 g. of potassium bromide, then 20 cc. of 10% sulfuric acid and 50 cc. of 0.1 N potassium bromate solution of known titer (organic solvent was not used). After two hours' standing in the dark the excess of bromine was measured iodimetrically. When the determinations were made with saturated bromine water, the procedure was as follows: 25 cc. of the stock solution was used

TABLE II

RESULTS OF DETERMINATIONS

Acid	Calculated iodine number	Found with Winkler's method	Free acid	Found with satd. bromine water	
				Potassium acid salt	Neutral salt
Crotonic	295	297			
Isocrotonic	295	297	...	...	...
Fumaric	218.8	7	106	193	216.7
Maleic	218.8	23	178	200	217.2
Lactone of 3-hydroxy-isocrotonic	302	trace	trace	...	187.0

---

[29] See Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," 1922.

either as such (free acid) or after neutralization with 0.1 *N* alkali (without indicator). To this was added 10 cc. of saturated bromine water of known titer, the solution was left to stand for two hours in the dark and the excess bromine then titrated (Table II).

The lactone of the 3-hydroxy-isocrotonic acid has a very inactive double bond; it seems to be a heterocyclic compound. It suffers a complicated rearrangement with alkali and has maximum ability to absorb bromine only immediately after saponification.

As a result of this preliminary study the following procedures for the control of oxidations of the acids listed above were adopted.

In the oxidation of fumaric and maleic acids two samples are taken out from time to time: one is neutralized in the presence of indicator for the determination of the acidity and the other is titrated with bromine water after it has been neutralized without using indicator.

In the oxidation of the 3-hydroxy-isocrotonic lactone a sample is taken and heated with an excess of 0.1 N alkali for five minutes on the water-bath; after the solution has been cooled, the excess of alkali is titrated with 0.1 N sulfuric acid, using a very small amount of phenolphthalein, and the solution is then titrated immediately with bromine water.

In the oxidation of crotonic and isocrotonic acids the samples are titrated with alkali for the acidity and with bromine water without neutralization.

If there is silver in the solution, it must be precipitated with sodium chloride solution before testing.

The presence of osmic acid in the bromine titrations does not give any trouble as it does not oxidize hydrogen bromide in weakly acid solutions.

In the perbenzoic acid oxidations the amount of the peracid is measured iodimetrically. If it is necessary to titrate with bromine water, the samples are very much (at least ten times) diluted, as the peracid quickly oxidizes hydrobromic acid.

Oxidation of Crotonic Acid with Perbenzoic Acid

(a) Oxidation in Chloroform Solution.—Ten g. of crotonic acid was dissolved in 500 cc. of water, and 84 cc. of chloroform which contained 24 g. of perbenzoic acid (50% excess) was added. The mixture was shaken at room temperature in the dark.

Time	Start	2 weeks	4 weeks	5 weeks
$CHCl_3$ soln., cc.	0.2	0.2	0.2	0.2
0.1 N $Na_2S_2O_3$ soln., cc.	6.95	4.40	2.80	2.40

Both aqueous and chloroform solutions now required a negligible amount of bromine water.

The chloroform layer was then separated from the aqueous layer and the former was washed with 100 cc. of water. The united aqueous solutions were concentrated at reduced pressure to 300 cc., extracted three times with 50 cc. of chloroform and the water completely removed by further distillation. The residue was dried at a temperature of 40° and a pressure of 2 mm. for several hours. The pale yellow, viscous sirup weighed 12.2 g. (88% of the theoretical). The sirup was dissolved in 14 cc. of ethyl acetate and cooled to 0°. Crystallization took place as soon as the glass wall was scratched and the solution was transformed into a white semi-crystalline mass. After six hours' standing in ice, the mass was subjected to suction filtration and the crystals washed with cold ethyl acetate and dried at 40°, finally in a vacuum desiccator over phosphorus pentoxide. A yield of 8.65 g. of white crystals (m. p. 80.5°) was obtained.

From the mother liquor there was obtained **0.2** g. more of pure crystals, making a total yield of **8.85** g. or **63.5%** of the theoretical.

The crystals were dissolved in **15** cc. of hot ethyl acetate, the solution treated with bone black and filtered hot by suction. The filtrate deposited as it cooled **7.4** g. of white crystals (m. p. 81.5°). A mixture of this acid with the acid obtained by the oxidation of isocrotonic acid with silver chlorate showed no depression of the melting point.

Titration. Subs., 0.3141, 0.3011: 25.85, 24.93 cc. of 0.1 N alkali (phenolphthalein). Calcd. mol. wt. for $C_4H_8O_4$: **120.06.** Found: **121.5, 120.7.**

The acid was found to be very soluble in water, alcohol, acetone and hot ethyl acetate, slightly soluble in cold ethyl acetate and ether, insoluble in chloroform and ligroin.

(b) Oxidation in Aqueous Solution.—Ten g. of crotonic acid was dissolved in **500** cc. of water which contained **4** g. of perbenzoic acid. The solution was allowed to stand at room temperature. During the course of two months a total of 20 g. of crystallized peracid was added from time to time, and after six weeks 100 cc. of ether. Even after two months there was still present about 20% of the crotonic acid. The oxidation was interrupted and the reaction mixture worked up as before. The yield was **8.5** g. of sirup. which gave **5.5** g. of crystals (m. p. **80.5")** in two crops, **40%** of the theoretical.

Oxidation of Isocrotonic Acid with Perbenzoic Acid

(a) Oxidation in Chloroform Solution.—Ten g. of pure, crystallizable isocrotonic acid (m. p. 15.5°) was dissolved in **200** cc. of water and **125** cc. of chloroform which contained **30** g. of perbenzoic acid was added. The mixture was shaken at room temperature in the dark.

After three weeks both aqueous and chloroform solutions required only a negligible amount of bromine water.

The reaction mixture was worked up in exactly the same manner as described above under the oxidation of crotonic acid. Thirteen g. of pale yellow sirup was obtained; 93% of the theoretical. This gave in two crops **8.75** g. of crystals (m. p. 73.5–74°) or 62.5% of the theoretical.

The crystals were recrystallized from hot ethyl acetate; **7.5** g. of crystals (m. p. **74–74.5°**) was obtained. A mixture of this acid with the acid obtained by the oxidation of the crotonic acid with chlorates showed no depression of the melting point. The solubility of the product is almost the same as that of the acid of m. p. **81.5".**

(b) Oxidation in Water Solution.—Three and a half g. of isocrotonic acid (m. p. **15.0")** was dissolved in **175** cc. of water which contained **1.5** g. of perbenzoic acid. The solution was allowed to stand at room temperature. During the course of three months a total of **10.5** g. of peracid was added from time to time. After six weeks **50** cc. of ether was added. The yield was **4.0** g. of sirup which gave **3.22** g. of crystals (m. p. 73.5–74°) in two crops, or **65%** of the theoretical.

Oxidation of Crotonic Acid with Chlorates. I. Barium Chlorate Oxidations

(A) Addition of Total Quantity of Chlorate in One Operation.—Twenty g. of crotonic acid was dissolved in one liter of water which contained **15.6** g. of barium chlorate (25% excess) and **2.5** cc. of a **1%** solution of osmic acid. The solution was kept at room temperature in the dark.

Time	Start	2 days	4 days	6 days
Solution, cc.	2	2	2	2
0.1 N alkali, cc.	4.65	4.30	3.75	3.50
Satd. bromine water, cc.	3.2	2.3	1.1	0.2

No pressure developed in the bottle. The solution was then separated by filtration from a small amount of crystals, which proved to be barium oxalate.

Anal. Subs., 0.3276: loss in weight at 150–160°, 0.0444; $BaSO_4$, 0.2917. Calcd. for $C_2O_4Ba\cdot 2H_2O$: H_2O, 13.78; Ba, 52.54. Found: H_2O, 13.56; Ba, 52.40.

The filtrate from the barium oxalate was extracted twice with 200 cc. of benzene; the water solution was then concentrated to a thin sirup at reduced pressure. The sirup was dissolved in one liter of water and the solution again subjected to distillation in order to remove all of the volatile acids. The residue of the second distillation was dissolved in 300 cc. of water and the excess of barium chlorate was reduced with sulfur dioxide gas. The barium sulfate was separated by filtration and the filtrate concentrated to two-thirds of its volume at reduced pressure. Then the sulfuric and hydrochloric acids were completely removed with barium hydroxide and silver oxide.

The purified solution, which contained the dihydroxybutyric acid and about 20% of the crotonic acid as chlorohydroxybutyric acid, was evaporated to a thick sirup and finally dried at a temperature of 40° and a pressure of 10 mm. for several hours. The yield was 22 g. of pale yellow sirup. This was dissolved in 20 cc. of absolute ethyl acetate and the solution cooled in ice. Crystallization began as soon as the glass walls were scratched. After twelve hours' standing in ice the crystals were separated by filtration, washed carefully with cold ethyl acetate and dried at 40°: Crop I, 8.4 g. of white crystals (m. p. 73.5°); Crop II (see later), 2.0 g. of white crystals (m. p. 72.5°); total, 10.4 g. of white crystals (m. p. 73°), or 38% of the theoretical.

These crystals were recrystallized from hot ethyl acetate and 9.0 g. of crystals (m. p. 74–74.5°) was obtained.

Titration. Subs., 0.2945, 0.3845: 24.31, 31.70 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_4H_8O_4$: 120.06. Found: 121.1, 121.3.

The mother liquor from Crop I was diluted with ethyl acetate to 50 cc. and was shaken once with 50 cc. of water. The two solutions were treated separately.

(a) Water Solution.—The solution was evaporated at reduced pressure and the residue dried and crystallized from ethyl acetate in the usual manner. Two g. of crystals (m. p. 72.5") was obtained (Crop II). They were united with Crop I.

(b) Ethyl Acetate Solution.—This was shaken twice with 20 cc. of water and the ethyl acetate layer dried with sodium sulfate, evaporated and the residue dried at 70° for several hours at reduced pressure. The yield was 1.75 g. of sirup, which did not crystallize. A sample of 0.1745 g. required 12.24 cc. of 0.1 N alkali and after saponification with 0.1 N alkali 11.47 cc. of 0.1 N silver nitrate; calcd. for chlorohydroxybutyric acid, $C_4H_7O_3Cl$: mol. wt., 138.5; Cl, 25.6. Found: mol. wt., 142; chlorine, 23.3.

About 20 g. of this crude chlorohydroxybutyric acid obtained from different experiments was dissolved in 50 cc. of water and the solution extracted twice with 150 cc. of ether. The residue obtained from the ethereal solution was dissolved in 50 cc. of water and the solution neutralized with zinc carbonate. The concentrated solution of the zinc salt deposited 2.0 g. of crystals after standing for three days in ice. A sample of 1.8 g. of the crystallized zinc salt was dissolved in 30 cc. of water, 20 cc. of 10% sulfuric acid was added and the solution extracted with ether, etc. The residue of the ether solution weighed 1.1 g. This was dissolved in 1 cc. of ether and crystallized in ice: 0.3 g. of white crystals (m. p. 76°) was obtained.

Anal. Subs., 0.0991: 6.98 cc. of 0.1 *N* alkali for free acid; 7.18 cc. of 0.1 *N* alkali and 7.22 cc. of 0.1 N silver nitrate for organically bound chlorine after saponification on the water-bath for fifteen minutes. Calcd. for $C_4H_7O_3Cl$: mol. wt., 138.5; Cl, 25.6. Found: mol. wt., 142; Cl, 25.8.

(B) Gradual Addition of Chlorate During Oxidation.—Twenty g. of crotonic acid was dissolved in one liter of water which contained 5 cc. of a 1% osmic acid solution.

Then in the course of three weeks 15.6 g. of barium chlorate was added in about 0.4-g. lots whenever the solution became brown. After four weeks the crotonic acid had entirely disappeared. The decrease in the initial acidity was about 24%. The reaction mixture was worked up as before. The yield of the oxidized product was 24.9 g. and that of the dihydroxybutyric acid (m. p. 72°) 13.5 g. or 48% of the theoretical. The amount of the chlorinated compound was a little less than under (A).

II. Oxidation with Potassium Chlorate

Twenty g. of crotonic acid was dissolved in one liter of water which contained 5 cc. of a 1% solution of osmic acid. Then in the course of three weeks 12 g. of potassium chlorate was added in about 0.3-g. lots whenever the solution became brown. After four weeks the oxidation was complete. There was a 24% decrease in the acidity. The solution was extracted with benzene and the excess of potassium chlorate was reduced with sulfur dioxide gas in the usual manner. The sulfuric acid was precipitated with barium hydroxide; the potassium chloride remained in solution. The residue from the distillation of the water solution was dissolved in 20 cc. of absolute alcohol and absolute ethyl acetate was added until no more precipitation occurred (about 600 cc. of ethyl acetate).

(a) Precipitate.—This was treated with 150 cc. of hot absolute alcohol and the potassium chloride removed by filtration in the hot. The filtrate contained only a trace of chlorine and deposited on cooling 10.9 g. of white crystals (m. p. about 104–106°, not sharp). The product was easily soluble in hot absolute alcohol, from which it may be recrystallized; it is insoluble in ethyl acetate.

Anal. Subs., 0.5121: 17.0 cc. of 0.1 N alkali; $KClO_4$, 0.2537. Calcd. for $C_4H_7O_4K \cdot C_4H_8O_4$: acid, 43.3; K, 14.05. Found: acid, 40.0; K, 13.98.

Three g. of the double salt was dissolved in 400 cc. of water and 11 cc. of N sulfuric acid was added. The solution was then distilled to dryness at reduced pressure, the residue was dissolved in ethyl acetate, etc., in the usual manner. Two and six-tenths g. of a crystalline mass was obtained which yielded 2.0 g. of crystals (m. p. 74°) in two crops.

(b) Ethyl Acetate Solution.—The residue obtained by the removal of the ethyl acetate at reduced pressure weighed 14.8 g., which gave 3.2 g. of crystals (m. p. 73") from ethyl acetate. The mother liquor of the crystals contained about 20% of the crotonic acid as chlorohydroxybutyric acid.

III. Oxidation of Crotonic Acid with Silver Chlorate

(A) Silver Chlorate in Excess.—Twenty g. of crotonic acid was dissolved in one liter of water which contained 18.3 g. of silver chlorate and 2.5 cc. of a 1% solution of osmic acid. The reaction mixture stood at room temperature. The precipitation of the silver chloride began immediately and the solution turned milky.

After 5 days a sample required only a negligible amount of bromine water. At the end of the oxidation there was a slight pressure in the flask. The silver chloride was separated by filtration. According to analysis it contained a small amount of silver oxalate.

The filtrate from the silver chloride was extracted with' benzene and evaporated at reduced pressure. A large amount of crystals appeared. These were dissolved in water and the distillation was repeated. The residue was treated with 100 cc. of absolute alcohol and the crystals were separated by filtration.

(a) Crystals.—These proved to be the silver salt of the dihydroxybutyric acid (m. p. 74°); weight, 4.5 g.

Anal. Subs., 0.9420, 0.4905: 41.40, 21.62 cc. of 0.1 *N* KCNS. Calcd. for $C_4H_7O_4Ag$: Ag, 47.54. Found: Ag, 47.4, 47.56.

Eight g. of this salt from different experiments was dissolved in water and the calculated amount of hydrochloric acid was added, etc.; yield, 4.0 g. of sirup, which gave 3.1 g. of crystals (m. p. 74°).

(b) Alcoholic Solution.—This was evaporated at reduced pressure, the residue treated with ethyl acetate, the solution filtered and the filtrate distilled to dryness. The pale yellow sirup which remained weighed 23 g. and gave 12.8 g. of crystals (m. p. 74°) in two crops from ethyl acetate; total yield (acid and silver salt) was 54% of the theoretical. The mother liquor of the crystals contained about 5% of the crotonic acid as chlorohydroxybutyric acid.

In other cases, when the silver salt was not separated and the oxidation lasted for about two weeks and somewhat more silver chlorate was used (20 g. of silver chlorate for 20 g. of crotonic acid), the yields of dihydroxybutyric acid (m. p. 74°) averaged 60% of the theoretical.

(B) Oxidation by Gradual Addition of Silver Chlorate.—Twenty g. of crotonic acid was dissolved in one liter of ice water which contained 10 cc. of a 1% osmic acid solution and little by little 18.0 g. of crystallized silver chlorate was added in about four weeks, while the solution was kept in ice water. The oxidation was rapid at the beginning; 0.5 g. of chlorate was added as a first portion; the solution became milky within a few minutes and turned brown in three hours. Then on every succeeding day for about two weeks, one g. of chlorate was added in 0.5-g. portions; the oxidation then became slower and 0.5 g. of chlorate was added whenever the solution turned yellow. Finally, the reaction mixture was removed from the ice-bath and allowed to stand at room temperature for a few days. After 18.0 g. of chlorate had been added, the solution remained colorless, showing that no more oxidizable substance was present.

There was no change in the initial acidity and no trace of crotonic acid, but a trace of chlorinated compound was found. The silver precipitate was separated by filtration and washed with dilute hydrochloric acid, giving 13.15 g. of silver chloride. A very small amount of oxalic acid was separated from the hydrochloric acid filtrate.

The filtrate from the silver chloride was distilled at reduced pressure, the excess of silver chlorate (about 0.5 g.) was reduced with sulfur dioxide gas, etc., in the usual manner. The residue from the water solution was a colorless, very viscous sirup which weighed 26.7 g.; 96% of the theoretical. The yield from ethyl acetate in three crops was 23.05 g. of crystals (m. p. 74°) or 82.5% of the theoretical.

The crystals were recrystallized from 40 cc. of ethyl acetate and yielded in two crops a total of 20.8 g. of crystals (m. p. 74.5–75°).

The non-crystallizable residue of the crude crystals weighed 2.7 g.

When the oxidation was carried out at room temperature in the manner described above and when half the amount of osmic acid was used, the yield was 92% of sirup and 70% of the dihydroxybutyric acid (m. p. 74°).

Oxidation of Isocrotonic Acid by Gradual Addition of Silver Chlorate

Six g. of pure isocrotonic acid (m. p. 15.0°) was dissolved in 300 cc. of ice water which contained 2.5 cc. of a 1% osmic acid solution. Then in four weeks 53 cc. of a 10% silver chlorate solution was added in 1.5-cc. portions while the solution was kept in an ice-bath in the dark, etc., as described in the silver chlorate oxidation of crotonic acid under (B). There was no change in the acidity and only a trace of chlorinated compound was found. The yield was 8.05 g. of colorless sirup or 96% of the theoretical. The sirup gave from ethyl acetate in two crops 6.88 g. of crystals (m. p. 81°) or 82%

of the theoretical. The product was recrystallized from 20 cc. of ethyl acetate; 6.0 g. of crystals (m. p. 81.5°) was obtained.

Oxidation of the Lactone of 3-Hydroxy-isocrotonic Acid with Silver and Barium Chlorates

(A) Silver Chlorate.—Ten g. of the lactone (m. p. 5.0°) was dissolved in 100 cc. of water which contained 5 cc. of a 1% osmic acid solution, and ten g. of silver chlorate was added in the course of two months. The reaction mixture stood at room temperature. In the first three additions 2 g. of chlorate was added; thereafter 0.5 g. of chlorate whenever the solution turned brown. At the end of the oxidation there was a slight pressure in the bottle. The titration showed that about 60% of free acid and 40% of lactone was present.

The silver chloride was separated by filtration (the silver precipitate did not contain any oxalate), the filtrate diluted to 250 cc.. extracted with benzene, distilled at reduced pressure to a thick sirup and finally the residue was dried at a temperature of 50° and a pressure of 2 mm. for several hours. The sirup contained only a trace of organically bound chlorine.

This sirup (13.3 g.) was dissolved in 15 cc. of absolute acetone and the solution cooled in ice. During six hours the solution deposited 7.1 g. of crystals (m. p. 89–90°).

The mother liquor was concentrated to a thick sirup, which was dried at a pressure of 2 mm. and a temperature of 70° for two hours. The residue gave 2.2 g. of crystals from absolute acetone. A third crystallization in the same way yielded 1.0 g. of crystals.

The final mother liquor was subjected to distillation at a temperature of 130–150° and a pressure of 1 mm. but suffered partial decomposition. The distillate gave 0.2 g. of crystals from absolute acetone. The total yield of crystallized product was 10.5 g. or 75% of the theoretical.

The crystals were dissolved in 100 cc. of hot absolute acetone, the solution was subjected to filtration in the hot and the filtrate concentrated to 30 cc. This solution deposited after ten hours' standing in ice 8.0 g. of crystals (m. p. 92°).

Two g. of crystals (m. p. 92°) was dissolved in 10 cc. of dilute nitric acid (sp. gr., 1.22) and the solution was kept at 60° for forty-five hours, that is, until evolution of brown fumes had ceased. The nitric acid was removed by distillation at reduced pressure in the usual manner. The crystalline residue was dissolved in 300 cc. of water, the solution neutralized with alkali, heated to boiling and a small amount of calcium acetate solution added until no more precipitation occurred. After ten minutes the calcium oxalate was removed by filtration in the hot. The calcium oxalate was dissolved in dilute hydrochloric acid and again precipitated in the usual manner. The precipitate was washed with hot water and then dried at 105° to constant weight; 0.34 g. of substance was obtained.

Anal. Subs. 0.3393: CaO, 0.1294. Calcd. for $CaC_2O_4 \cdot H_2O$: CaO, 38.34. Found: CaO, 38.14.

The filtrate of the calcium oxalate was acidified with dilute hydrochloric acid and concentrated to 75 cc. at reduced pressure. Then the solution was heated, neutralized and the calcium mesotartrate precipitated with an excess of calcium acetate. After twenty-four hours the precipitate was separated by filtration, washed with warm water and dried in the air for eighteen hours. Three g. of air-dried calcium salt was obtained.

Anal. Subs., 0.2329: loss in weight at 180°, 0.0521; ash, 0.0538. Calcd. for $C_4H_4O_6Ca \cdot 3H_2O$: H_2O, 22.32. Found: 22.37. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.76.

This shows that the oxidation yielded, except for a small quantity of oxalic acid, exclusively mesotartaric acid.

(B) Barium Chlorate.—Ten g. of lactone (m. p. 5.0') was dissolved in 100 cc. of water which contained 5 cc. of a 1% solution of osmic acid and 9.2 g. of barium chlorate was added during two months, etc., in just the same manner as described under (A). The yield was 12.7 g. of sirup, which gave 9.1 g. of crystals (m. p. 90°), or 64% of the theoretical. There was found only a trace of organically bound chlorine.

Oxidation of Maleic Anhydride with Barium and Silver Chlorates

(A) Barium Chlorate.—Ten g. of maleic anhydride (m. p. 54°) was dissolved in 500 cc. of water which contained 12.0 g. of barium chlorate and 2.5 cc. of a 1% osmic acid solution. The mixture stood at room temperature. At the beginning the solution became yellow; the color later disappeared. The oxidation was complete in two months; the solution required only a negligible amount of bromine water. There was no change in acidity.

The solution was then extracted with benzene, the excess of barium chlorate reduced with sulfur dioxide gas and the sulfuric and hydrochloric acids were removed in the usual manner. The purified water solution was evaporated at reduced pressure and the crystallized residue dried at a temperature of 40° and a pressure of 8 mm. for three hours. The yield was 15.0 g. of white crystals which contained, according to titration, 13.9 g. of mesotartaric acid or 91% of the theoretical.

The water solution of the acid did not give a precipitate with calcium sulfate water, showing the absence of racemic tartaric acid. The product did not contain a trace of chlorine and required only a trace of bromine water after neutralization.

The oxidation of the maleic anhydride therefore gave exclusively mesotartaric acid.

(B) Silver Chlorate.—Ten g. of maleic anhydride was dissolved in 500 cc. of water which contained 12.0 g. of silver chlorate and 2.5 cc. of a 1% solution of osmic acid. The oxidation was complete in two months, the solution requiring a negligible amount of bromine water. There was a 26% decrease in the acidity. The reaction mixture was worked up as described under (A). The pure solution of the oxidized product did not give a precipitate with calcium sulfate water and contained, according to titration, 10.3 g. of mesotartaric acid or 67% of the theoretical.

The author wishes to thank Dr. J. Stieglitz, Dr. J. W. E. Glattfeld and Dr. J. K. Senior for help in the prosecution of this work and the International Education Board for the financial support which made it possible.

Summary

1. The oxidation of crotonic and isocrotonic acids with perbenzoic acid is described. Crotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) with a yield of 63.5% of the theoretical. Isocrotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 74–75') with a yield of 62.5%.

2. The oxidation of crotonic and isocrotonic acids with silver chlorate in the presence of osmic acid as a catalyst was carried out. Crotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 74–75') with a yield of 82.5%. Isocrotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) with a yield of 82.5%.

3. A study of the results of the oxidation of crotonic acid with various chlorates in the presence of osmic acid is described. It was shown that in the chlorate oxidations the reduction of chlorates proceeds through the lower oxides of chlorine and the mechanism of these oxidations is discussed.

4. The most probable structure of the two theoretically possible *dl*-1,2-dihydroxybutyric acids is suggested.

5. A modified procedure for the oxidation of the lactone of 3-hydroxy-isocrotonic acid with silver and barium chlorates is given.

6. The results of a comparative study of the oxidation of maleic anhydride with silver and barium chlorates are given.

CHICAGO, ILLINOIS

[CONTRIBUTION WOM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 189]

ELECTRON DISPLACEMENT IN CARBON COMPOUNDS. V. THE ADDITION OF HYDROGEN CHLORIDE TO 3-ETHYL-2-PENTENE[1]

BY HOWARD J. LUCAS

RECEIVED JULY 23, 1928 PUBLISHED JANUARY 8, 1929

In order to account for the products formed when strong acids add to derivatives of ethylene, investigators have proposed different hypotheses. Markownikoff[2] many years ago laid down the rule that when hydrogen bromide or other similar compound adds, the negative atom goes to that unsaturated carbon atom which is joined to the larger number of other carbon atoms. But there are many exceptions to this rule, the best recognized being acrylic acid, which with hydrogen bromide forms β-bromo-acrylic acid instead of a-bromo-acrylic acid.

An extension of the Lewis theory of molecular structure[3,4] offers another explanation for these phenomena based upon the electron attraction of radicals.

Making use of the formula diagrams, it is evident that a comparison of these values for H, CH_3 and C_2H_5 is all that need be considered. If the usually accepted order of electron attraction, *viz.*, $H > CH_3 > C_2H_5$, is correct,[4] then carbon atom C—2 must have a stronger attraction for the four electrons of the double bond than C—3, since its other four electrons are attracted more strongly by H and CH_3 than are the other four electrons about C—3.[5] Thus C—2 is negative with respect to C—3 (b) and when

---

[1] Presented at the Claremont meeting of the Pacific Section, American Association for the Advancement of Science, June 15, 1928.

[2] Markownikoff, *J. prakt. Chem.*, 48, 345, 452 (1892).

[3] Lewis, THIS JOURNAL, 38, 762 (1916).

[4] Lucas and Moyse, *ibid.*, 47, 1459 (1925); Lucas, *ibid.*, 48, 1827 (1926). See also Kharasch and Grafflin, *ibid.*, 47, 1948 (1925); Kharasch and Marker, *ibid.*, 48, 3130 (1926).

[5] From their work on the polarization of the isomeric heptanes, Smyth and Stoops, THIS JOURNAL, 50, 1889 (1928), conclude that any electron shifts existing in these hydrocarbons are so small that they have no appreciable effect upon properties. They also maintain that these and other results provide strong evidence against the assumption

hydrogen chloride adds the halogen should go largely to *C—3,* producing 3-chloro-3-ethylpentane.

(a) Electron displacement structure (b) Polarity due to electron displacement

Polarity and electron structures of 3-ethyl-2-pentene

The hypothesis of alternate polarity would predict that the isomeric 2-chloro-3-ethylpentane would be the principal product.

Hydrogen chloride was selected as the addendum because (a) the aliphatic chlorides are more stable than the bromides and iodides, a very important factor when dealing with easily dissociated secondary and tertiary halides,[6] and (b) the bromides of the higher alcohols boil at temperatures close to those of the alcohols themselves, whereas the chlorides boil considerably lower.

In order to obtain the desired chlorides it was first necessary to prepare the corresponding alcohols, 3-ethyl-2-pentanol and 3-ethyl-3-pentanol (triethylmethanol). The former was obtained from 3-ethyl-2-pentanone by reduction with sodium according to the procedure used for other alcohols[7] and the latter from ethyl bromide and diethylketone by the Grignard method. In carrying out the synthesis of these two alcohols the author was assisted by W. P. Baxter, whose valuable aid is hereby gratefully acknowledged.

The preparation of the two chlorides, 2-chloro-3-ethylpentane and 3-chloro-3-ethylpentane, was accomplished at room temperature by stirring the corresponding alcohol with concentrated hydrochloric acid and zinc chloride and removing the acid layer every few hours. This process resembles the method of Norris and Taylor,[8] who heat the reacting substances, but is a modification which seemed desirable in order to avoid elevated temperatures at which isomeric change would be more rapid. Such a change has been observed in the case of certain alkyl halides.[9] Zinc chloride is a necessary catalyst for the reaction between hydrochloric acid and 3-ethyl-2-pentanol, which undergoes only a 75% conversion

---

of any considerable variation in the position of the electron pairs even in other series of compounds. See also Smyth, *ibid.,* 46, 2151 (1924); Krchma and Williams, *ibid.,* 49, 2408 (1927).

[6] Whereas the chloride obtained from 3-ethyl-2-pentanol could be distilled at atmospheric pressure with only slight decomposition, the bromide evolved hydrogen bromide strongly when heated.

[7] Wislicenus, *Ann.,* 219,309 (1883).

[8] Norris and Taylor, THIS JOURNAL, **46,753** (1924).

[9] Wischnegradsky, *Ann.,* 190,342 (1878), observed that in the reaction of secondary iso-amyl alcohol with hydrochloric and hydriodic acids, the products are tertiary halides, not secondary. Michael and Zeidler, ibid., **393,** 81 (1912), and Michael, Scharf and Voigt, THIS JOURNAL, 38, 653 (1916), observed that pure isobutyl bromide slowly changed to the tertiary compound.

after forty hours without zinc chloride, but is completely converted after sixteen hours in the presence of zinc chloride. Although no attempt was made to determine the minimum time necessary for complete conversion, it is probable that a shorter time would suffice. In view of the fact that tertiary butyl alcohol reacts readily with concentrated hydrochloric acid alone,[10] it is probable that the tertiary heptyl alcohol would have behaved in a similar fashion. However, in order to obtain complete conversion the tertiary chloride was prepared in the same way as the secondary, that is by the use of zinc chloride at room temperature. The attempt to extend the method to primary *iso*butyl alcohol was unsuccessful, no chloride resulting even after several days.

The unsaturated hydrocarbon, 3-ethyl-2-pentene, is readily obtained from the tertiary alcohol, 3-ethyl-3-pentanol, by heating at 100° under a reflux cooler with anhydrous oxalic acid. It combines with hydrogen chloride dissolved in glacial acetic to give a quantitative yield of a heptyl chloride, the properties of which are given in Table I.

In Table I are listed the two heptyl alcohols, the heptene, the two heptyl chlorides, the reaction product and some of the physical properties of these compounds. The boiling points, taken with short Anschiitz thermometers, needed no correction and are given as read; the densities were determined on small samples by the plummet method and are corrected for buoyancy; the refractive indices were determined with an Abbk re-

TABLE I

PHYSICAL CONSTANTS

	Roiling points (corr.)			Densities, ;! Dried over		Refractive Indices	
	50 mm.	90 mm.	743 mm.	K_2CO_3	P_2O_5	n_D^{20}	n_D^{25}
1 3-Ethyl-2-pentanol	82.0–82.5	....	151.0–151.5	0.8359	....	1.4284	1.4264
2 3-Ethyl-3-pentanol	72.5–73.5	83.5–84.0	140.5–141.5	.8438	....	1.4305	1.4281
3 3-Ethyl-2-pentene	....	....	95.0–95.5 (745)	.7190	....	....	1.4128
4 2-Chloro-3-ethylpentane	60.0–63.5	77.0–77.5	142.5–143.0	.8911	0.8874	1.4319	1.4295
5 3-Chloro-3-ethylpentane	83.0–83.5 (100)	78.5–79.0 (93)	143.0–144.0 (decompn.)	.8945	.8917	1.4334	1.4311
6 Reaction product	....	78.0–79.0	....	.8948	.8916	....	1.4311

Constants previously given are for 1, b. p. 148–152°; d°, 0.8531 (ref. 14); for 2, b. p. 141–143° (ref. 17a), 142° (764 mm.) (ref. 17b), 141–148" (746 mm.)(ref. 17f), 130–140" (ref. 17g); d_{20}^{20}, 0.84016 (ref. 17a); for 3, b. p., 97--98"; d_0^{20}, 0.72225; d_0^{15}, 0.72544 (ref. 17d); for 5, b. p., 143–144°; d_4^{25}, 0.8644; n_D^{25}, 1.43276 (ref. 17e).

---

[10] Davis and Murray, *Ind.* Eng. Chem., 18,844 (1926).

fractometer which was checked at frequent intervals against the standard prism,

The close agreement in the properties of the reaction product and of 3-chloro-3-ethylpentane indicates that this substance constitutes 95–100% of the **material** formed when hydrogen chloride in glacial acetic acid adds to 3-ethyl-2-pentene. The reaction therefore follows the course predicted on the assumption that the electron attractions of the atoms and radicals attached to the unsaturated carbon atoms are in the order $H > CH_3 > C_2H_5$. The course is similar to that between this heptene and sulfuric acid, the product of which was assumed to be the tertiary alcohol, since it was completely decomposed on repeated distillation at atmospheric pressure.[11]

Experimental Part

3-Ethyl-2-pentanone (Unsymmetrical Diethylacetone).—This was obtained in 30% yield by passing a mixture of acetic and diethylacetic acids over thorium oxide at 410–430° and in 31% yield through the acetoacetic ester synthesis in which the diethylacetoacetic ester first produced was decomposed by barium hydroxide according to the general method of Wislicenus.[12] A modification was introduced by using, in place of the 0.25 N solution of barium hydroxide, one approximately twice as concentrated. The material obtained by the pyrolysis method boiled at 136–140" and had a refractive index, n_D^{20}, of 1.4076; that by the decomposition of the ester boiled at 136–137° under a pressure of 745 mm.[13] and had a refractive index. n_D^{20}, of 1.4073.

3-Ethyl-2-pentanol.—This has been obtained, along with other products, by the action of chloro-acetone upon ethylmagnesium bromide.[14] The reduction of 3-ethyl-2-pentanone by means of metallic sodium according to the method used for the reduction of other ketones[7] using, however; twice the amount of sodium necessary for the reaction and diluting the ketone with four times its volume of ether in order to decrease the amount of pinacol produced, gave the desired alcohol in 70% yield and the corresponding pinacol in 8% yield. Complete reduction of the ketone can be brought about by using the excess of sodium recommended. The alcohol, 48 g., distilled at 82.0–82.5° (corr.) under a pressure of 50 mm. and at 151–151.5° (corr.) under 743 mm. without decomposition. It has a pronounced camphor-like odor.

4,5-Dimethyl-3,6-diethyl-4,5-octanediol.—The pinacol obtained in the reduction of 3-ethyl-2-pentanone after two crystallizations from alcohol melted at 100.7–101.2° (corr.). Three determinations of its molecular weight by the micro method of Smith and Young[15] gave 235,[16] which agrees well with 230, the value calculated from $C_{14}H_{30}O_2$.

3-Ethyl-3-pentanol.[11,17]—From 86 g. (1 mole) of diethyl ketone, b. p. 101.2–103.2°,

---

[11] Brooks and Humphrey, THIS JOURNAL, 40,835 (1918).

[12] Wislicenus, *Ann.*, 190, 250 (1877); 206,308 (1880).

[13] Other values for the boiling point are 137.5–139°, Franklin and Duppa, *Ann.*, 138,212 (1866); 138° (760 mm.), Clarke, *Am. Chem. J.*, 39,574 (1908); 138°, Tiffeneau and Dorlencourt, *Compt. rend.*, 143, 127 (1906).

[14] Fourneau and Tiffeneau, *Compt. rend.*, 145,437 (1907).

[15] Smith and Young, *J. Biol. Chem.*, 75,289 (1927).

[16] Molecular weight determinations were made by Mr. W. G. Young.

[17] (a) Barataeff and Saytzeff, *J. prakt. Chem.*, [2] 34, 463 (1886); (b) Weigert, *Ber.*, 36, 1004 (1903); (c) Ipatieff, *J. Russ. Phys.-Chem. Soc.*, 27, 363 (1895), *Jahresb.*, 1895, 971; (d) Saytzeff, *J. prakt. Chem.*, [2] 57, 38 (1898); (e) Schreiner, *ibid.*, [2] 82,

110 g. (1 mole) of ethyl bromide and 24.5 g. (1 mole) of magnesium in 200 cc. of absolute ether, there was obtained 70 g. (63% yield) of crude 3-ethyl-3-pentanol distilling at 68–72° under 49 mm. The material from two batches was fractionally distilled under a pressure of 50 mm. to prevent decomposition. The fractionation was performed six times, the refractive index being used as a check on the purity. During the last three distillations this value was practically constant. The boiling point of the final product, which has a pronounced camphor-like odor much resembling that of the isomeric alcohol, was 72.5–73.5' (corr.) at 50 mm., 83.5–84.0° (corr.) at 90 mm. and 140.5–141.5° (corr.) at 743 mm. It had refractive indices as follows: n_{D}^{20}, 1.4305 and n_{D}^{25}, 1.4281.

2-Chloro-3-ethylpentme.—The chlorides were prepared at room temperature of approximately 22° in order to decrease the possibility of isomeric change.[9] This chloride was prepared by stirring 10 g. (0.09 mole) of 3-ethyl-2-pentanol with 3 successive portions of 21 g. (0.2 mole) of concentrated hydrochloric acid and 22 g. (0.2 mole) of anhydrous zinc chloride over a period of fourteen hours, renewing the acid at approximately five-hour intervals. The product was shaken with small quantities of water in order to remove most of the acid and dried with anhydrous potassium carbonate. Two fractional distillations, the first at 90 mm. over a range of 70–77° and the second at 50 mm. over a range of 62.0–62.5° (corr.), gave 3.7 g. (35% yield) of product. The two fractions of each distillation differed but slightly in refractive index, the best values being n_{D}^{20}, 1.4318 and n_{D}^{25}, 1.4299. At the end of both distillations there was no tendency for the thermometer thread to rise, indicating absence of any higher boiling material such as the alcohol. The density, d_{25}^{25}, was 0.8911. After standing over phosphorus pentoxide for twenty-four hours, n_{D}^{25} was 1.4295.

When the alcohol was stirred for forty hours with concentrated hydrochloric acid in the proportions given above with replacement every six or seven hours but without the zinc chloride, the product after shaking out with water and drying over potassium carbonate was by weight only 75% converted and had a refractive index, n_{D}^{20}, 1.4293. When distilled at 50 mm. the temperature was slightly higher than before, *viz.*, 63–65', and the indices of the different fractions differed by 0.0011. It was evident that the reaction had not gone to completion even after forty hours.

3-Chloro-3-ethylpentme.—This was prepared by stirring at room temperature 11.6 g. (0.1 mole) of 3-ethyl-3-pentanol with four successive portions of 21 g. (0.2 mole) of concentrated hydrochloric acid and 22 g. (0.2 mole) of anhydrous zinc chloride over a period of eighteen hours, renewing the acid at approximately five-hour intervals. After separating the heptyl chloride, washing five times with water and drying over potassium carbonate, the weight of the crude product was 12.6 g., a yield of 94%. In the operations which followed, drying over phosphorus pentoxide, distilling under a pressure of 100 mm. at 83.0–83.5° (corr.) and drying again over both drying agents, the refractive index was not changed, n_{D}^{25} being 1.4311. Standing for twenty-four hours over phosphorus pentoxide did not change the value.

After the chloride had been distilled at reduced pressure, distillation at atmospheric pressure could be carried on with but slight decomposition. Without a previous distillation the undistilled material evolved hydrogen chloride copiously when heated, probably due to the catalytic influence of suspended matter.[18]

3-Ethyl-2-pentene.—This was obtained by heating equal weights of 3-ethyl-3-pentanol and anhydrous oxalic acid on a boiling water-bath under a reflux cooler for five hours.[11,17d] The hydrocarbon was distilled over, separated from the water, refluxed with metallic sodium and finally distilled from the sodium, coming over at 95–96°.

---

292 (1910); (f) Mazurewitsch, J. *Russ. Phys.-Chem. Soc.*, 42, 1582 (1910); *Chem. Cent.*, 1911, *I*, 1500; (g) Davies and Kipping, J. *Chem. Soc.*, 99, 298 (1911).

[18] Rice, THIS JOURNAL, 48, 2099 (1926).

After refluxing again with sodium, the material distilled at 95.0–95.5° (corr.) at 745 mm. The yield was 84%.

Hydrogen Chloride and 3-Ethyl-2-pentene.—Dry hydrogen chloride was passed into 30 g. of glacial acetic acid, the solution was then cooled by ice and water and the gas was passed in until saturation was reached, 3 g. (0.08 mole) dissolving. To this was added 10.0 g. (0.10 mole) of 3-ethyl-2-pentene and additional hydrogen chloride was passed in until a total of 5 g. (0.14 mole) had dissolved. The mixture stood overnight at 8-10', ice and water were then added and the chloride layer was washed five times with cold water. The weight of the undried chloride layer was 13.3 g., theoretical yield, 13.2 g. This indicated that addition was practically quantitative. After drying over anhydrous potassium carbonate the refractive index, n_D^{25}, was 1.4311 and the density, d_{25}^{25}, was 0.8951. The material distilled completely at 78-79' under 90-91 mm. pressure. The refractive index was unchanged and the density was 0.8948. After standing for twenty-four hours over phosphorus pentoxide the refractive index was still 1.4311.

The refractive index of the reaction product was identical with that of 3-chloro-3-ethylpentane, but the density was too high, being slightly above the value for this chloride. The three materials were allowed to stand for about a month over phosphorus pentoxide, the densities then being, 2-chloro-3-ethylpentane, 0.8874, 3-chloro-3-ethylpentane, 0.8917, and the reaction product, 0.8916. This brought all of the densities down and left the value for the reaction product slightly less than that of 3-chloro-3-ethylpentane. The refractive indices were not again determined although it is possible. that they may have changed. The properties of the reaction product are thus practically identical with those of 3-chloro-3-ethylpentane.

Summary

The heptyl chlorides, 2-chloro- and 3-chloro-3-ethyl pentane have been prepared in a pure state from the corresponding alcohols at room temperature by stirring with concentrated hydrochloric acid and zinc chloride. Some physical properties have been determined.

Hydrogen chloride in glacial acetic acid reacting with 3-ethyl-2-pentene gives a heptyl chloride which is practically pure 3-chloro-3-ethylpentane.

The product formed agrees with the prediction made on the assumption that the electron attractions of hydrogen, methyl and ethylene are in the order $H > CH_3 > C_2H_5$, and not with the hypothesis of an alternately polarized carbon chain.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLVII. SYNTHESIS OF POLYPEPTIDE HYDANTOINS FROM 2-THIOHYDANTOIN-3-ACETIC ACID[1]

BY ALICE G. RENFREW[2] AND TREAT B. JOHNSON

RECEIVED JULY 26, 1928 PUBLISHED JANUARY 8, 1929

In the study of new organic principles applicable for internal antisepsis we inaugurated three years ago a new feature by introducing into our researches on germicides an investigation of some phenolic derivatives of hydantoin. Having reliable knowledge of the fact that the hydantoin cycle is a non-toxic organic construction and one which is also very resistant to the action of ferments and bacterial enzymes,[3] we concluded that it would be of special interest to determine whether it would be feasible to utilize the hydantoin nucleus as a vehicle for transporting antiseptic groupings in the body. Johnson and Coghill[4] prepared, in the preliminary work, a series of mono- and di-phenol derivatives of hydantoin with the phenolic grouping —C_6H_4OH substituted on both carbon and nitrogen atoms of the hydantoin cycle. A preliminary bacteriological examination of several of these derivatives has already been reported. None thus far examined exhibited an antiseptic activity comparable to phenol. The new combinations did not prove of practical utility as germicidal agents on account of their insolubility in water. The toxicity of the aromatic phenol group, however, was reduced by coupling the benzene nucleus with the hydantoin.

In continuing this work we sought to incorporate changes in constitution which would be expected to increase the solubility of our compounds and at the same time lead to constructions favorable for pharmaceutical application. We therefore turned our attention to a study of certain simple, phenolic constructions combined with the polypeptide hydantoin nucleus. It was felt that a study of the effect of introducing acid groupings on nitrogen would be beneficial; we therefore undertook the preparation of new combinations of this type. The grouping which we selected to increase the solubility of our phenolic compounds was the acid radical —H_2CCOOH. This has been incorporated by substitution in positions

---

[1] This investigation was supported in part by a grant from the Therapeutic Research Committee of the Council on Chemistry and Pharmacy of the American Medical Association.

[2] Constructed from a dissertation presented by Alice Gertrude Renfrew to the Faculty of the Graduate School of Yale University, in June, 1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Lewis, *J. Biol. Chem.*, 13, 347 (1912); 14, 245 (1913).

[4] Johnson and Coghill, THIS JOURNAL, 47, 184 (1925); also Coghill, *ibid.*, 47, 216 (1925).

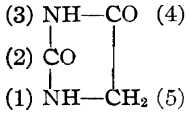
1 and 3 of the hydantoin cycle. In this paper we shall confine our discussion to some derivatives of hydantoin-3-acetic acid, I, and its corresponding sulfur analog, II. The results of our study of derivatives of hydantoin-1-acetic acid will be reported in a later paper.[5]

It has been the experience of this Laboratory that aldehyde condensations are more readily effected with 2-thiohydantoins than with the oxygen analogs. Regarding the influence of sulfur in position 4 or in dithiohydantoins on the course of such condensation reactions we have no knowledge. Johnson and his co-workers have made comparative studies of both hydantoin and 2-thiohydantoin in condensations with various aldehydes[6] The greater activity of the thiohydantoin also characterizes the condensation of hydantoin cycles containing substituents in the 1- and 3-positions of the ring. 1-Phenyl-2-thiohydantoin and 1,3-diphenyl-2-thiohydantoin were condensable with aldehydes without difficulty.[7] Using the corresponding oxygen derivatives, Wheeler and Hoffmann[8] were unsuccessful in effecting similar condensations, although Johnson and Hadley[9] later actually succeeded in condensing 1,3-diphenylhydantoin with benzaldehyde. Thus far no successful condensations of 1-phenylhydantoin with aldehydes have been reported.

The condensations that have been applied successfully with hydantoin-3-acetic acid and its sulfur analog are described in detail in the Experimental Part of this paper, and are illustrated structurally herewith. The three aldehydes used were p-anisaldehyde, salicylaldehyde and piperonal. By inspection of the formulas it will be observed that all of these new products have been represented structurally as cyclic methylene condensation reactions. This is an important conclusion of our work as both the 2-thiohydantion-3-acetic acid, II, and its oxygen analog, I, contain two methylene radicals theoretically capable of condensing with aldehydes. In no case, however, have we obtained any evidence that the methylene radical in the acyclic acetic acid group undergoes a condensation reaction with an aldehyde. Also in no aldehyde condensation reaction did we succeed in revealing a single new case of geometric

---

[5] The system used for numbering the positions of the hydantoin ring, as represented, will be adopted throughout this and following papers. It is in accord with the system of classification in use in Beilstein's "Handbuch der Organische Chemie," and in the subject index of *Chemical Abstracts.* A method of numbering which has been widely used in the past is one in which the numerical assignments to the two nitrogen atoms of the cycle are reversed.



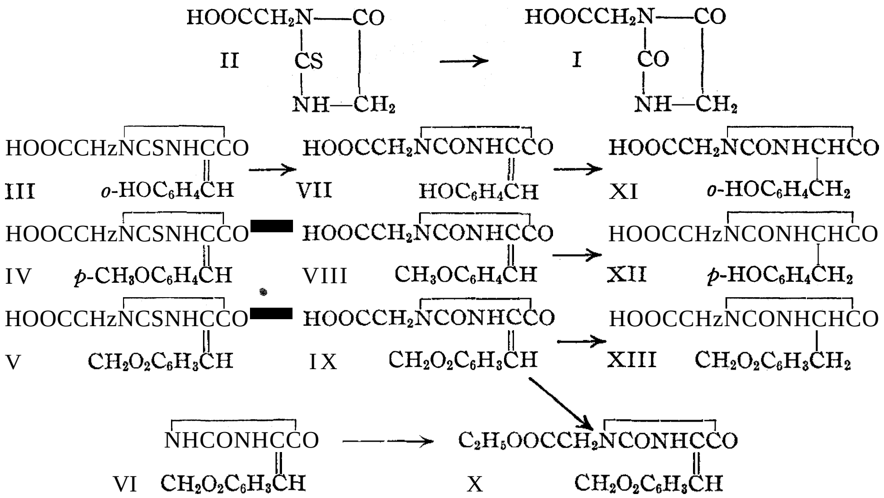
$$\begin{array}{lll} (3)\ NH & - & CO\ (4) \\ (2)\ CO & & \\ (1)\ NH & - & CH_2\ (5) \end{array}$$

[6] Johnson and Scott, THIS JOURNAL, 37,1846 (1915); Johnson, Pfau, and Hodge, *ibid.,* 34, 1041 (1912); Johnson and Bengis, ibid., 35, 1606 (1913); Johnson and Wrenshall, *ibid.,* 37,2133 (1915).

[7] Wheeler and Brautlecht, *Am. Chem. J., 45,446* (1911).

[8] Wheeler and Hoffmann, *ibid.,* 45,368 (1911).

[9] Johnson and Hadley, THIS JOURNAL, 37,171 (1915).



isomerism, despite the fact that the reaction products were carefully studied.

An interesting result worthy of special mention is the fact that most of the condensations applied with the three aldehydes and the hydantoin-3-acetic acids, I and II, in the presence of sodium acetate gave the sodium salts of the condensation products, notwithstanding the fact that all the condensations were carred out in glacal acetic acid solution. The two exceptions were the reaction products resulting from condensation of anisaldehyde and piperonal with 2-thiohydantoin-3-acetic acid. Here the free substituted hydantoin-acetic acids were obtained.

The condensations between 2-thiohydantoin-3-acetic acid, II (or its oxygen analog, I), with aldehydes serve also another useful purpose in that they make it possible to establish conclusively the structure of alkylation products of simple aldehyde-hydantoins when the alkylation method is used in the preparation of polypeptide hydantoin configurations. For example, the structure of the alkylation product X is established by the fact that the same derivative is formed by esterification of the hydantoin IX. It is a common experience that hydantoins of Type VI undergo substitution first in position 3 when subjected to the conditions of an alkylation reaction.

Experimental Part

2-Thiohydantoin-3-acetic acid, $HOOCCH_2NCSNHCH_2CO$.—The acid is easily obtained in a yield of 85–90% of the theoretical according to the method of Johnson and **Renfrew.**[10]

2-Thio-5-panisalhydantoin-3-aceticAcid, $HOOCCH_2NCSNHC{=}(CHC_6H_4OCH_3)CO$.—This hydantoin is formed by digesting thiohydantoin-3-acetic acid (5 g.) with *p*-anisal-

---

[10] Johnson and Renfrew, THIS JOURNAL, **47,** **240** (1925).

dehyde (5.5 g.) in the presence of 6 g. of anhydrous sodium acetate, 10 cc. of glacial acetic acid and 3 cc. of acetic anhydride. After heating the above mixture in an oil-bath for ten minutes at 250–260°, the fluid changed to a magma of the solid hydantoin. A further 10 cc. of glacial acetic acid was then added and the heating continued for two hours, when the condensation was apparently complete. The hydantoin was separated by filtering the reaction mixture while hot and washing with water and alcohol to remove impurities. A yield of 6.7 g. was obtained, corresponding to 80% of the theoretical. The hydantoin is purified by crystallization from alcohol or acetic acid and melts at 280–282°.

Anal. Calcd. for $C_{13}H_{12}O_4N_2S$: N, 9.59. Found: N, 9.63, 9.67.

5-*p*-Anisalhydantoin-3-acetic acid, $\mathrm{HOOCCH_2\overline{NCONHC{=}(CHC_6H_4OCH_3)C}O}$.—This hydantoin-acetic acid has been described previously by Johnson and Hahn,[11] and recently by Granacher and Landolt.[12] The same hydantoin is also obtained by desulfurizing the above 2-thiohydantoin with chloro-acetic acid. A mixture of our product with a specimen of the original hydantoin showed no change in melting point, namely, 269–271°.

In an effort to accumulate further comparative data on the reactivity of the methylene group in nitrogen-substituted hydantoins, this hydantoin was also synthesized by a third method, namely, by condensing anisaldehyde with hydantoin-3-acetic acid. Reaction was brought about by digesting in a mixture of glacial acetic acid and acetic anhydride in the presence of anhydrous sodium acetate. The reaction was complete after refluxing in an oil-bath for three hours. After cooling, the acetic acid solution was diluted with water, when the condensation product separated. This was identified as the sodium salt of anisalhydantoin-3-acetic acid, corresponding in yield to 41% of the theoretical. The salt was initially colorless but after recrystallization from water it separated in green plates which deposited an alkaline residue when burned on platinum foil. This salt was not very soluble in water. These properties characterize the monosodium salt of this hydantoin, which has been studied by Hahn and Burt,[13] thus excluding the possibility of the condensation product being an acyclic hydantoin acid derivative. An excess of hydrochloric acid added to an aqueous solution of the sodium salt produced a heavy precipitate of the corresponding acetic acid. The acid showed a melting point in accordance with that already recorded. With recovery of some salt from filtrates, the total yield of condensation product was 51% of the theoretical. With slight variations in technique this same synthesis has been reported recently by Granacher and Landolt[12] as giving a yield of 57%. This unsaturated hydantoin is reduced smoothly to *p*-hydroxybenzylhydantoin-3-acetic acid when digested with hydriodic acid and red phosphorus.[11]

Salicylalhydantoin-3-Acetic Acid Derivatives

2-Thio-5-salicylalhydantoin-3-acetic Acid, $\mathrm{HOOCCH_2\overline{NCSNHC{=}(CHC_6H_4OH)C}O}$.—This compound is easily formed by applying a condensation reaction with salicylic aldehyde and thiohydantoin-3-acetic acid. The reagents required are used in the following proportions: thiohydantoin-acetic acid, 10 g., salicylaldehyde, 10 g., sodium acetate 12 g., and glacial acetic acid, 30 cc. After heating this mixture for ten to fifteen minutes at 150–155°, the liquid became completely saturated with the condensation product and finally completely solidified. Water was then added to bring it to a volume of

---

[11] Johnson and Hahn, THIS JOURNAL, 39, 1255 (1917).

[12] Granacher and Landolt, *Helv. Chim. Acta*, 10, 799 (1927).

[13] Hahn and Burt, THIS JOURNAL, 39, 2468 (1917).

50 cc. and the insoluble condensation product was separated by filtration. This was identified as the sodium salt of 2-thio-salicylalhydantoin-3-aceticacid and we obtained a yield of 14 g. The salt crystallizes from hot water and is converted into its corresponding acid by the action of hydrochloric acid. The yield of hydantoin was 96% of the theoretical. It was purified by crystallization from glacial acetic acid and melted with decomposition at 253–254°.

Anal. Calcd. for $C_{12}H_{10}O_4N_2S$: N, 10.07. Found: N, 10.12, 10.20.

Salicylalhydantoin-3-acetic acid, $HOOCCH_2\overline{NCONHC{=}(CHC_6H_4OH)C}O$.—Ten grams of the above 2-thiohydantoin compound was suspended in a solution containing 30 g. of chloro-acetic acid in 30 cc. of water. After boiling for five hours, the reaction was complete and the hydantoin had separated. This compound is very insoluble in acetic acid, 120 cc. dissolving less than 2 g. of the hydantoin. It crystallized from boiling acetic acid in light yellow, prismatic crystals melting at 273–274° with decomposition.

Anal. Calcd. for $C_{12}H_{10}O_5N_2$: N, 10.68. Found: N, 10.50, 10.56.

Esterification of this hydantoin-acetic acid with ethyl alcohol gives an ester melting at 164° (uncorr.). An attempt was made to prepare this compound by alkylation of salicylalhydantoin[14] with ethyl chloro-acetate, but the reaction does not take place smoothly and a gummy product is formed from which it is very difficult to separate the ethyl ester.

o-Hydroxybenzylhydantoin-3-acetic Acid, $HOOCCH_2\overline{NCONHCH(CH_2C_6H_4OH)C}O$.—This polypeptide hydantoin was first approached by heating salicylalhydantoin-3-acetic acid with hydriodic acid and red phosphorus. This treatment led to the formation of a gummy product which was extremely difficult to purify. It was found that the reduction could be accomplished by using hydriodic acid alone. The unsaturated hydantoin was suspended in five times its weight of hydriodic acid and the mixture carefully heated, but never allowed to boil. After complete solution the mixture was allowed to stand for a few minutes and the acid then diluted with water. Part of the polypeptide hydantoin crystallized directly from this diluted solution; the remainder was obtained by allowing the filtrate to concentrate in a vacuum over sodium hydroxide. The yield of crude reduction product was about 75% of the theoretical. The hydantoin was purified by crystallization from hot water and separated in the form of rosets melting at 189–190°.

Anal. Calcd. for $C_{12}H_{12}O_5N_2$: N, 10.60. Found: N, 10.59, 10.60.

As would be expected this polypeptide hydantoin gives a positive Jaffé picric acid reaction. A red-brown layer develops very rapidly when the test is performed by the modified method of Brand and Sandberg.[15]

2-Thio-5-piperonal-hydantoin-3-aceticAcid, $HOOCCH_2\overline{NCSNHC{=}(CHC_6H_3O_2CH_2)C}O$.—This compound was obtained in a yield of 90% of the theoretical by condensation of piperonal with 2-thiohydantoin-3-aceticacid. The acid, which was the initial reaction product in this case, crystallizes from boiling acetic acid in small, glistening, yellow crystals which melt with decomposition at 291°.

Anal. Calcd. for $C_{13}H_{10}O_5N_2S$: N, 9.02. Found: N, 8.83, 8.97.

5-Piperonalhydantoin-3-acetic acid, $HOOCCH_2\overline{NCONHC{=}(CHC_6H_3O_2CH_2)C}O$.——The above sulfur hydantoin was desulfurized by refluxing for about thirty hours with

---

[14] Johnson and Scott, THIS JOURNAL. 37, 1846 (1915).

[15] Brand and Sandberg, J. *Biol. Chem.*, 70,381 (1926).

a 50% solution of chloro-acetic acid. The solid never completely dissolved but it gradually became lighter in color and formed hard, compact crystals which settled to the bottom of the flask. The hydantoin separated from acetic acid in the form of lemon-yellow rosets which melted at 275–276°.

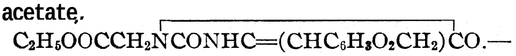
Anal. Calcd. for $C_{13}H_{10}O_6N_2$: N, 9.65. Found: N, 9.78, 9.94.

To prove that this compound was a derivative of piperonal-hydantoin rather than a possible condensation product involving a reaction of the methylene radical in the acetic acid group of the hydantoin-3-acetic acid, the acid was esterified with ethyl

$$H_2CO_2C_6H_3CH{=}C(COOH)NCONHCH_2CO$$

alcohol. This ester was found to be identical with the hydantoin-ester formed by direct alkylation of the sodium salt of piperonalhydantoin with ethyl chloro-acetate.

Ethyl **5-Piperonal-hydantoin-3-acetate**,



$$C_2H_5OOCCH_2NCONHC{=}(CHC_6H_3O_2CH_2)CO$$

.—Ten grams of piperonal-hydantoin[5] was suspended in 100 cc. of absolute alcohol containing in solution 1.3 g. of metallic sodium. After digesting for forty-eight hours, two molecular equivalents of ethyl chloro-acetate was added and the digestion continued for two days. The solution was filtered hot and the insoluble residue was triturated with dilute hydrochloric acid, when a small quantity of crystalline material was obtained having the properties of piperonylic acid. From the alcohol solution the above ester separated in the form of prisms melting at 159–160°. It was insoluble in alcohol. When mixed with the ester prepared by esterification of piperonalhydantoin-3-acetic acid, the melting point was not changed.

Anal. Calcd. for $C_{15}H_{14}O_6N_2$: N, 8.80. Found: N, 8.81.

Summary

1. It has been shown that hydantoin-3-acetic acid and its sulfur analog both condense with aldehydes.
2. The cyclic methylene group is the reactive position in the hydantoin.
3. The sulfur hydantoin reacts more favorably with aldehydes than the hydantoin-3-acetic acid.
4. The three aldehydes, anisaldehyde, salicylaldehyde and piperonal gave condensation products which do not exhibit geometric isomerism.
5. The polypeptide hydantoins containing free phenolic groups are being examined to determine their germicidal value and toxicity.

NEW HAVEN, CONNECTICUT

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

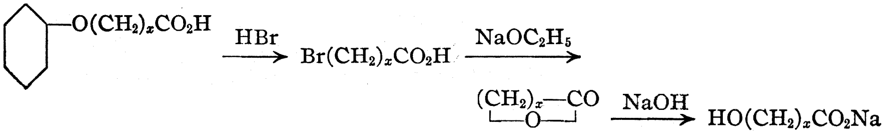
THE PREPARATION OF THE SODIUM SALTS OF OMEGA-HYDROXYBUTYRIC, -VALERIC AND -CAPROIC ACIDS

BY C. S. MARVEL AND E. R. BIRKHIMER

RECEIVED JULY 30, 1928 PUBLISHED JANUARY 8, 1929

Several studies have been made of the hydroxy and amino acids in an attempt to find whether or not they give the same end products in metabolism in the animal organism. In order to gain further information concerning this problem, the preparation of the salts of some w-hydroxy acids was undertaken so that they might be compared with the w-amino acids which have recently been studied by Corley.[1]

The general procedure which was used for the preparation of these compounds can be illustrated by the following reactions



Although these reactions are not essentially new, the methods have not been described in sufficient detail to make possible the easy production of any considerable amounts of these compounds.

y-Phenoxybutyric acid was prepared by the method of Lohmann[2] except that the hydrolysis was carried out under a reflux condenser and not in closed tubes. y-Bromobutyric acid was obtained from it by the method devised by Merchant, Wickert and Marvel[3] for converting phenoxy acids to the corresponding bromo acids. The bromo acid was converted to y-butyrolactone by the method which Cloves[4] has described for the preparation of 6-valerolactone from 8-bromovaleric acid. The lactone was saponified in the usual way with dilute sodium hydroxide solution.

8-Valerolactone was prepared by the same series of reactions, starting with 6-phenoxyvalericacid, and then hydrolyzed to give sodium δ-hydroxyvalerate. However, when Cloves' method of preparing a lactone was applied to ϵ-bromocaproic acid, a very poor yield of ϵ-caprolactone was obtained. This material was apparently a compound of the type $[O(CH_2)_5COO(CH_2)_5CO]_x$, since on hydrolyzing with aqueous hydroxide solution it gave a salt which by analysis agreed with sodium hydroxycaproate.

---

[1] Corley, J. *Biol.* Chem., **70,** 99 (1926).

[2] Lohmann, Ber., 24, 2640 (1891).

[3] Merchant, Wickert and Marvel, THIS JOURNAL, 49, 1828 (1927).

[4] Cloves, *Ann.,* 319, 367 (1901).

Experimental Part

γ-Phenoxybutyric Acid.—A mixture of 500 *g.* of phenoxypropyl cyanide and 2500 cc. of concentrated hydrochloric acid (sp. gr., 1.19) was boiled under a reflux condenser for about five hours. The phenoxybutyric acid was extracted with benzene, the benzene evaporated and the product distilled under reduced pressure. The yield was 340 g. (61% of the theoretical amount) boiling at 192–197° (18 mm.).

y-Bromobutyric Acid.—A mixture of 340 g. of γ-phenoxybutyric acid and 550 cc. of 48% hydrobromic acid was placed in a 1-liter round-bottomed flask attached to a 1-meter fractionating column by means of a mercury seal. The reaction mixture was heated to such a point that the temperature of the vapors at the top of the column was about 120°. After about five hours no more phenol was distilling. The reaction mixture was diluted with water and the y-bromobutyric acid was extracted with ether. The product was distilled under reduced pressure. The yield was 220 g. (70% of the theoretical amount) of γ-bromobutyric acid, b. p. 124–127° (7 mm.).

γ-Butyrolactone.—To a solution of 7.8 g. of sodium in 500 cc. of absolute alcohol was added 60.5 g. of γ-bromobutyric acid. The reaction mixture was boiled under a reflux condenser for about five hours. During this time sodium bromide separated. The alcohol was distilled from a steam-bath and the lactone was separated from the sodium bromide by extraction with ether. The ether was evaporated and the lactone distilled under ordinary pressure. The yield was 21.2 g. (67% of the theoretical amount) of a product boiling at 202–206°; sp. gr. $^{28}_{28}$, 1.1054; $n^{26.5}_{\mathrm{D}}$, 1.4343.

Sodium **γ-Hydroxybutyrate.**—A mixture of 16.3 g. of γ-butyrolactone and 7.4 g. of sodium hydroxide dissolved in 30 cc. of water was boiled under a reflux condenser for about three hours. At the end of this time more water was added to dissolve the salt and the solution was filtered and evaporated to dryness under reduced pressure. The salt was recrystallized from alcohol. The yield was 11.5 g. (40% of the theoretical amount).

Anal. Subs., 0.2106: Na_2SO_4, 0.1171. Calcd. for $C_4H_7O_3Na$: Na, 18.25. Found: Na, 18.02.

δ-Valerolactone.—δ-Valerolactone was obtained in 58% yield from δ-bromovaleric acid by the method of Cloves." It boiled at 215–220° at atmospheric pressure; sp. gr. $^{20}_{20}$, 1.1130; n^{20}_{D}, 1.4600.

Sodium **δ-Hydroxyvalerate.**—This material was prepared by the method used for the corresponding butyric acid derivative. From 11 g. of lactone and 4 g. of sodium hydroxide in 20 cc. of water there was obtained 6.6 g. (47% of the theoretical amount) of product.

Anal. Subs., 0.2140: Na_2SO_4, 0.1085. Calcd. for $C_5H_9O_3Na$: Na, 16.43. Found: Na, 16.42.

Sodium **ε-Hydroxycaproate.**—To a solution of 9 g. of sodium in 500 cc. of absolute alcohol was added 77 g. of e-bromocaproic acid. The solution was boiled under reflux for about five hours and then the alcohol was distilled and the residue in the flask extracted with ether. The ether was evaporated and an attempt was made to distil the residue. About 10 g. of material which seemed to be slightly impure e-caprolactone was obtained, boiling at 135–140° (35 mm.). It gave a slight test for bromine; sp. gr. $^{24}_{24}$, 1.0306; n^{24}_{D}, 1.4481.

There was considerable residue (25–30 g.) left in the distilling flask which did not distil when heated to about 200° under 35 mm. pressure. This residue was hydrolyzed by boiling with an aqueous solution of about 6 g. of sodium hydroxide. This solution was decolorized with decolorizing carbon (Norite), filtered and evaporated to dryness. The residue was recrystallized from alcohol. In this manner 14.5 g. of the sodium salt was obtained.

Anal. Subs., 0.2012: Na_2SO_4, 0.0943. Subs., 0.1987: CO_2, 0.3126; H_2O, 0.1277. Calcd. for $C_6H_{11}O_3Na$: Na, 14.93; C, 46.75; H, 7.14. Found: Na, 15.05; C, 46.81; H, 7.14.

Summary

Convenient procedures for the preparation of the sodium salts of the ω-hydroxy derivatives of butyric, valeric and caproic acids have been described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

SALTS OF AROMATIC NITRILES. II. POTASSIUM PHENYLACETONITRILE

BY MARY M. RISING, IRVING E. MUSKAT AND EDMUND W. LOWE

RECEIVED AUGUST 3, 1928 PUBLISHED JANUARY 8, 1929

There appeared recently a paper[1] by one of the present authors and Dr. Tsoh-Wu Zee in which were discussed the method of preparation and the behavior of sodium phenylacetonitrile, $[(C_6H_5)HC{=}C{=}N]Na$ and $[(C_6H_5)(CN)HC]Na$, and of sodium α-phenylbutyronitrile,[2] $[(C_6H_5)(C_2H_5)C{=}C{=}N]Na$ and $[(C_6H_5)(C_2H_5)(CN)C]Na$. The paper was accompanied by a statement to the effect that the purity and identity of these salts, which were obtained a number of times by Rising and Zee, were established conclusively from the analytical data and the reactions of the compounds, but that since the departure of Dr. Zee for China it had proved so far impossible to repeat his work and obtain the salts again in pure form.

In view of the experimental difficulties encountered in obtaining the sodium salts by the workers who followed Zee, a study of the potassium salts of phenylacetonitrile and α-phenylbutyronitrile was undertaken, and the present paper describes the preparation of potassium phenylacetonitrile, $[(C_6H_5)HC{=}C{=}N]K$, and $[(C_6H_5)(CN)HC]K$, and its conversion into a-phenylbutyronitrile in fairly good yield by treatment with ethyl iodide. The method used by Zee to obtain the sodium salts has been modified slightly and a method of purification of the potassium salt has been developed which will undoubtedly prove useful for other salts of this variety.

A few weeks after the publication of our last report on the sodium salts, the attention of one of the present authors was called by F. W. Upson and T. J. Thompson to a paper of theirs[3] which appeared in 1922 upon

---

[1] Rising and Zee, THIS JOURNAL, 50, 1699 (1928).

[2] This salt was described in an earlier paper by Rising and Zee, *ibid.*, 49, 541 (1927).

[3] Upson and Thompson, *ibid.*, 44, 181 (1922).

"The Preparation and Properties of Several Phenyl Alkyl Succinic Acids," at the end of which these authors describe, incidentally to the main theme of their work, the interesting behavior of a substance, not obtained by them in pure form, produced by the reaction of sodium amide upon phenylacetonitrile in ether. The properties of this substance led Upson and Thompson to conclude that it was sodium phenylacetonitrile, of nitride structure, $(C_6H_5)HC{=}C{=}NNa$. It is a source of great satisfaction to us to find that the conclusions of these workers regarding the structure of the salt are thus in agreement with our own. The results of their work and of ours present striking confirmation of the theory first proposed by Nef and Hesse[4] with regard to the structure of salts of organic nitriles. Upson and Thompson also suggest that an imide form of phenylacetonitrile, $(C_6H_5)HC{=}C{=}NH$, is an intermediate compound in certain condensation reactions, undergoing "rearrangement" to the nitrile form, $(C_6H_5)H_2C(CN)$, in the course of these reactions. An analogous rearrangement of the imide form of the dinitrile of malonic acid, $(CN)HC{=}C{=}NH$, to the nitrile form, $(CN)H_2C(CN)$, was previously proposed by Nef and Hesse. We regret that we failed to give credit in our previous papers to Upson and Thompson for their work in this field. Their paper had escaped our notice due to the two facts that no reference to their observations was included in the title of their paper, and that the indexes of Chemical *Abstracts* and other literature contained no reference to this part of their work.

Rising and Zee obtained sodium phenylacetonitrile in pure form;' they found interesting evidence for the Nef theory of bivalent carbon in the nature of the decomposition products of the salt with acid, and explained the behavior of this salt and of its homolog, sodium α-phenylbutyronitrile, in the reactions studied, upon the assumption of nitride–carbide tautomerism, obviously an extension of the Nef theory with regard to the tautomerism of hydrocyanic acid, the parent substance of nitriles; they also made suggestions regarding the role of sodium phenylacetonitrile in the aldol-like condensations described by von Meyer[5] and others.6 Work along these lines is being continued by Rising, the results to be reported in due time.

Experimental Part

Potassium Phenylacetonitrile $(C_6H_5)HC{=}C{=}NK$ and $(C_6H_5)(CN)HCK$.—This salt was prepared by the treatment of potassium powder with phenylacetonitrile in dry ether in an atmosphere of nitrogen, according to the equation

$$2(C_6H_5)CH_2CN + 2K \longrightarrow 2(C_6H_5)HC{=}C{=}NK + H_2 \qquad (1)$$

The salt can be obtained in pure condition only when the most rigorous precautions are

---

[4] Hesse, Doctor's "Dissertation," University of Chicago, 1896.

[5] E. von Meyer, J. *prakt. Chem.*, 22, 262 (1880); 38, 336 (1895); 52, 81 (1895).

[6] Holtzwart, *ibid.*, 38, 343 (1889); 39, 230 (1889); Wache, *ibid.*, 39, 245 (1889).

taken to exclude moisture and carbon dioxide; hence it has seemed best to describe the procedure used in some detail.

Apparatus.—The reaction vessel was a 200-cc. flask carrying a reflux condenser; in the top of the condenser was placed a stopper carrying a tube of calcium chloride, an inlet tube for nitrogen reaching to the bottom of the reaction flask and a dropping funnel closed by means of a tube of calcium chloride. It is of the utmost importance that this apparatus be thoroughly dried. For this purpose a stream of dry nitrogen was drawn through it for forty-eight hours, the apparatus being heated during this time.

Reagents.—The nitrogen used for drying all apparatus was purified by being drawn first through two vessels of alkaline pyrogallol, then over calcium chloride, next through concentrated sulfuric acid and finally over phosphorus pentoxide. The ether which served as the reaction medium was washed with water, placed once over calcium chloride and then twice over bright sodium. After the ether was distilled from the sodium the last traces of water were removed by treatment with sodium-lead alloy. Kahlbaum's phenylacetonitrile, of boiling point 230–231° (uncorr.), and of known purity, was used. Potassium powder was prepared as follows: small squares of freshly cut potassium, weighed under dry xylene, were placed in the reaction flask already described, which contained 30 cc. of xylene (thiophene-free, and dried over sodium-lead alloy). The flask, loosely stoppered, was warmed until the potassium melted; the flask was then tightly closed, and shaken vigorously with a vertical movement until the molten metal was converted into an exceedingly fine powder. The xylene was decanted, the metal was washed very thoroughly with dry ether and finally covered with a layer of dry ether.

Preparation of Potassium Phenylacetonitrile.—Potassium dust (4.2 g.), covered with 30 cc. of ether, was placed under the reflux condenser described. The reaction apparatus was then swept out with nitrogen. Phenylacetonitrile (14 g.), used in 11% excess of the calculated amount to force all of the potassium to react and dissolved in ether to make 60 cc., was allowed to drop slowly into the reaction flask from the dropping funnel. As the reaction began, hydrogen was evolved, a bulky yellow precipitate formed and the ether boiled. When no more hydrogen was evolved, the reaction mixture was warmed for half an hour. The product of the reaction was sticky and could not be readily removed from the flask; the ether was therefore decanted from it, and the residue was washed rapidly several times with ether. The flask and contents were then placed in a vacuum desiccator over phosphorus pentoxide and the last of the ether was drawn off by suction. As the ether was removed the salt swelled and became brittle. The crude product sometimes contained unused potassium metal. Usually, however, the potassium content was somewhat low, due probably to the fact that the excess of nitrile used was not completely removed from the sticky mass. The yield of the salt obtained was 10 g., or 60% of the theoretical. Some loss of product occurred because it could not be removed completely from the reaction flask; the yield was also somewhat lowered due to the fact that some of the potassium dust was lost in the process of washing it with ether.

Purification of Potassium Phenylacetonitrile.—The crude salt was purified as follows: 10 g. of it was treated with 150 cc. of dry benzene in a dry flask in an atmosphere of nitrogen, whereupon much of the crude product dissolved. The benzene solution of the salt was separated from the residue by filtration, a stream of nitrogen being meanwhile allowed to play over the surface of the solution. Following filtration, the benzene solution was treated with dry, low-boiling ligroin to reprecipitate the salt, which was separated by filtration through silk, being kept in an atmosphere of nitrogen during the filtration. The salt was washed several times with ligroin and quickly put into a desiccator over phosphorus pentoxide. The salt, now pure, was kept in an atmosphere of nitrogen until analyzed.

Anal. Subs. 0.1025, 0.1298: K_2SO_4, 0.0571, 0.0721. Subs., 0.3444, 0.2476: N_2, 27.70, 20.20 cc. (22°, 746.5 mm.) (over 50% KOH). Subs., 03073, 0.3594: CO_2, 0.6963, 0.8141; H_2O, 0.1080, 0.1255. Calcd. for KC_8H_6N: K, 25.19; N, 9.03; C, 61.86; H, 3.89. Found: K, 24.97, 24.92; N, 8.95, 9.06; C, 61.79, 61.77; H, 3.90, 3.88.

Behavior of Potassium **Phenylacetonitrile.**—The crude salt is a dark yellow, crystalline substance, becoming a lighter yellow after recrystallization. It is exceedingly sensitive to traces of water and acids, which decompose the salt with the formation of hydrocyanic acid It reacts with ethyl iodide to form a-phenylbutyronitrile, as follows

$$(C_6H_5)HC{=}C{=}NK \rightleftarrows (C_6H_5)(CN)HCK \qquad (2)$$

$$(C_6H_5)(CN)HCK + C_2H_5I \longrightarrow (C_6H_5)(CN)HC(C_2H_5) + KI \qquad (3)$$

For the preparation of a-phenylbutyronitrile by this method the salt was prepared in the usual way, the quantities of reagents being those previously specified, and was treated, without being separated from the reaction mixture, with ethyl iodide (18 g.), a 7% excess. The procedure and course of the reaction resemble that described in a previous paper[1] for the preparation of a-phenylbutyronitrile from sodium phenylacetonitrile. In the present case, however, the yield of nitrile was much better, being 10 g., or 64.4% of the theoretical yield calculated from the amount of potassium used.

Summary

1. The preparation of potassium phenylacetonitrileis reported.
2. The identity of the salt was established by analysis and by its reactions.
3. Its decomposition by acid into hydrocyanic acid indicates a nitride structure for the salt $[(C_6H_5)HC{=}C{=}N]K$.
4. Its conversion into α-phenylbutyronitrile by treatment with ethyl iodide indicates that the salt also exists in a carbide form (tautomeric with the nitride), $[(C_6H_5)(CN)HC]K$.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

CONCENTRATION OF HYDRAZINE HYDRATE SOLUTIONS

BY CHARLES D. HURD AND C. W. BENNETT

RECEIVED AUGUST 3, 1928 PUBLISHED JANUARY 8, 1929

Usually, aqueous solutions of hydrazine contain less than 30% of available hydrazine (40–45% hydrazine hydrate), since this concentration may be realized by refluxing[1] a mixture of water (75 parts), hydrazine sulfate (200 parts) and sodium hydroxide (160 parts), and then distilling. For many purposes such a solution of hydrazine hydrate is satisfactory. When more concentrated solutions are desired, the expedient is usually adopted of starting similarly but with less water, or with a minimum volume of water and considerable alcohol.[2] Such devices are far from satisfactory owing to poor yields.

---

[1] "Organic Chemical Reagents," 3, 40 (1921), University of Illinois Bulletin, Vol. 19, No. 6, Oct. 9, 1921.

[2] Vanino, "Handbuch der Präparativen Chemie," F. Enke, Stuttgart, 1913, Vol. I, p. 114.

In recent years, many substances have been satisfactorily dehydrated by distilling them in the presence of an immiscible liquid. It seemed not unlikely that a solution of hydrazine hydrate might be concentrated by such distillation methods and, indeed, such was found to be the case. The method is extremely simple and any degree of concentration up to about 95% of hydrazine hydrate is attainable. It is necessary merely to add a definite quantity of xylene to the dilute hydrazine hydrate solution in a distilling apparatus and heat it until the xylene has distilled away. The residue in the distilling flask, which contains most of the original hydrazine hydrate in concentrated form, may be distilled to a water-clear liquid if desired. The xylene and water which comprise the original distillate are easily separated. The aqueous portion contains varying amounts of hydrazine, which is readily recoverable; as would be expected, the xylene portion contains almost no hydrazine. Toluene may be used instead of xylene, but it is somewhat less efficient. Benzene effects but slight concentration and, therefore, is not to be recommended. Undoubtedly, other immiscible liquids with vapor pressures comparable to that of xylene would be found equally satisfactory and perhaps some would be preferable.

Some of the results may be briefly summarized. With equal parts (150 g. each) of xylene and a 41.8% solution of hydrazine hydrate, one distillation was found to effect a concentration (in 87% yields) to a hydrazine hydrate solution of about 65% strength. By taking 200 g. of xylene (with 150 g. of 41.8% hydrazine hydrate solution), one distillation brought about a change in concentration, in 64% yield, to a hydrazine hydrate solution of 82.7% strength. The latter boiled at 116–119°. The aqueous distillate which was removed by the xylene in the first experiment weighed 62.5 g. and contained 10% of hydrazine hydrate; in the second case it weighed 85 g. and contained 13% of hydrazine hydrate. Concentrations beyond 83% were effected by continued distillation with xylene, but in no case was it found possible to exceed 95–96% by this method. To obtain the latter concentration from a 33% hydrazine hydrate solution in one operation, 5 parts of the latter was distilled with 13 parts of xylene. The residual material, which represented only 12% of the original hydrazine content, boiled at 118–119° and analyzed for 95.4–95.8% of hydrazine hydrate. Although there was some loss, most of the remaining hydrazine was to be found in the aqueous layer of the distillate.

Metathetic Methods for the Liberation of Hydrazine

To liberate hydrazine from a salt such as hydrazine hydrochloride, two modifications of the double decomposition reaction have been recorded. The more customary of these two utilizes sodium hydroxide in water solution, and the alternative procedure makes use of sodium methylate[3] in methanol solution: $NaOCH_3 + N_2H_5Cl \longrightarrow N_2H_4 + CH_3OH + NaCl$. Water and methanol, respectively, contaminate the hydrazine in these two processes. With the purpose of producing uncontaminated hydrazine by a simple procedure, the following three metathetic methods were studied.

$NaNH_2 + N_2H_5X$ into $N_2H_4 + NaX + NH_3$
$CaC_2 + 2N_2H_5X$ into $2N_2H_4 + CaX_2 + C_2H_2$
$Al_4C_3 + 12N_2H_5X$ into $12N_2H_4 + 4AlX_3 + 3CH_4$
(In these reactions X represents chloride or sulfate)

Calcium carbide and hydrazine sulfate failed to interact up to 260°, except for a slight decomposition of the sulfate into free sulfur. The dihydrochloride (of hydrazine) made an explosion, and yielded a very small amount of liquid with an acetylene odor. The only apparent reaction between the dihydrochloride and aluminum carbide was the thermal decomposition of the hydrazine salt, apparently into hydrogen chloride, ammonium chloride, nitrogen and hydrogen. The reaction of sodamide with hydrazine salts under widely varying conditions was found to proceed with explosive violence[4] if undiluted. The use of the hydrocarbons "Nujol" (mineral oil) or xylene as reaction media effectually did away with the explosions, but failed to effect anything but trivial yields of hydrazine. It is quite possible that good results would have been obtained in liquid ammonia as solvent, but we did not try this.

Experimental Part

Solutions of hydrazine hydrate were prepared by the method given in Organic Chemical Reagents.' The hydrazine content of the solutions was determined by titration in acid solution (containing bromide ion) at 60° with 0.1 N potassium bromate solution according to the method of Kurtenacker and Wagner.[5] Three drops of a sulfuric acid solution of indigo was used as an indicator, the color changing from blue through green to yellow at the end-point.

Distillation of Hydrazine Hydrate Solution with Benzene

A mixture of 100 cc. of hydrazine hydrate solution (24% N_2H_5OH) and 200 cc. of benzene was distilled in the manner later described under toluene and xylene. The temperature of the vapors was 69–71° throughout the distillation. When all the benzene had distilled, it was found that only 8 cc. of water of 1.66% hydrazine hydrate content was also in the distillate. The residue of hydrazine hydrate solution in the distilling flask was found to contain 27% of hydrazine hydrate by weight. The benzene was also analyzed but was found to contain practically no hydrazine.

Concentration of Hydrazine Hydrate Solutions with Toluene

A mixture of 95 g. of hydrazine hydrate solution containing 24.6% of hydrazine hydrate by weight and 100 cc. of toluene was distilled using a 500-cc. flask fitted with a

---

[3] De Bruyn, *Rec. trav. chim.*, **13,** 433 (1894); L. U. Spence, Master's "Dissertation," Northwestern University, 1925.

[4] Possibly due to sodium hydrazide. See Stollé, *J. prakt. Chem.*, **83,** 200 (1911); Ebler, *Ber.*, 43, 1690 (1910).

[5] Kurtenacker and Wagner, *Z. anorg. Chem.*, 120, 265 (1921).

cork and a Hempel column of beads. The dimensions of the column were 35 mm. diameter and 17 cm. length. Prom the top of this column a side arm led through a condenser into a receiver. Wherever corks were exposed to hydrazine vapors, they were protected by tin foil. In the distillation the mixture came over at 85–86°, and when all of the toluene had distilled, there was about 20 cc. of water with it. This aqueous layer contained 2.7% of hydrazine hydrate by weight, and the aqueous residue contained 30.6%. The analytical data in these typical cases are given for reference.

Anal. 0.4570 g. of substance consumed 10 cc. of $KBrO_3$ solution, 1 cc. of which was equivalent to 0.00125 g. of N_2H_5OH. Pound: 2.7% of hydrazine hydrate. Subs., 0.1242; $KBrO_3$ solution, 30.4 cc. Found: hydrazine hydrate, 30.6.

The toluene was returned to the flask and the distillation repeated. Again 20 cc. of water was obtained with the same percentage of hydrazine hydrate, namely, 2.7%; the residue was nearly 40%. Again repeating this process, the residue of 25 g. analyzed for 61–61.5% of hydrazine hydrate and the aqueous distillate contained 2.8%. Again the toluene was returned and the distillation repeated. This time the mixture distilled at 89–90". In this case, the aqueous distillate weighed 12 g., and analyzed for about 12% hydrazine hydrate content. The residue was 68% hydrazine hydrate. By returning the toluene and redistilling, it was found that the next distillation temperature of the toluene–water–hydrazine mixture was 94–95°. The distillate (aq. layer) contained 47.6% of hydrazine hydrate by weight, and the residue (5 g.) 86% of hydrazine hydrate. This residue, on fractionation, gave 2.25 g. of a clear liquid which boiled at 117–119°. Analysis before and after fractionation gave values which were almost identical.

It will be shown directly that xylene effects this concentration, and even a greater concentration much more readily, and, therefore, is to be recommended in preference to toluene.

Concentration of Hydrazine Hydrate Solutions with Xylene

Preparation of 65% Hydrazine Hydrate.—A mixture of 150 g. of 41.8% hydrazine hydrate solution and 150 g. of xylene was distilled in the same apparatus as with the benzene and toluene. The distillation consumed only fifteen minutes and the vapors came over from 92–100°. All of the xylene and 62.5 g. of water came over. The watery portion of the distillate analyzed 10.5% by weight of hydrazine hydrate, whereas the residual solution in the flask, which weighed 85 g., analyzed for 65.2%. In other words, about 87% of the original hydrazine hydrate still remained in the concentrated residue.

Preparation of 82% and of 95% Hydrazine Hydrate Solutions.—The only difference from the preceding method was that a greater quantity of xylene was employed. These results are listed in Table I.

TABLE I

CONCENTRATION OF HYDRAZINE HYDRATE SOLUTIONS BY DISTILLING WITH XYLENE

Xylene used, g.	Orig. hydrazine hydrate soln. Wt., g.	Orig. hydrazine hydrate soln. N_2H_5OH, %	Dist. Temp., °C.	Xylene distd., g.	Final hydrazine hydrate soln. Aqueous distillate Wt., g.	Final hydrazine hydrate soln. Aqueous distillate N_2H_5OH, %	Final hydrazine hydrate soln. Residue Wt., g.	Final hydrazine hydrate soln. Residue N_2H_5OH, %
150	150	41 8	92–100	150	62.5	10.5	85	65.2
200	150	41 8	90–105	200	85	13	53[a]	82.2
650	250	33.1	90–96	178	63	1.7	[b]	..
...	Continued		96–101	129	51	12.8	..	..
...	distillation		101–105	220	72	46.1		..
...			105–107.5	36	15	75.1	15[c]	94.7

[a] The 53 g. of material was redistilled without xylene. The first small portion, which was oily, was discarded. Forty-eight g. of a water-clear liquid, b. p. 116–119°,

was obtained. Its hydrazine hydrate content was 82.7%. This concentrated solution represents about two-thirds of the original hydrazine content. Although there is some loss, much of the remaining third is readily recoverable from the first aqueous distillate.

values not determined because the distillation was uninterrupted until a temperature of **107.5**" was reached.

[c] The 15 *g.* of **94.77,** concentration was redistilled without xylene to obtain 10.5 g. of a fraction which boiled at 118–119°, and which analyzed for nearly **96%** of hydrazine hydrate **(95.4** and **95.4% in** two determinations). The yield of **10.5** *g.* of this high concentration represents about **12%** of the quantity of hydrazine hydrate that was in the original dilute solution. Although there is some loss by retention in the column of beads, and some actual loss, much of the remaining hydrazine is to be found in the "aqueous distillate."

Other attempts to obtain higher than 95–96% hydrazine hydrate by this method were not successful.

Summary

Dilute hydrazine hydrate solutions may be readily concentrated to solutions of 65% strength by distilling them with an equal weight of xylene until all the hydrocarbon is removed. By beginning with more xylene and distilling similarly, concentrations up to 95–96%, but apparently not higher, may be effected in a single operation. Toluene is considerably less efficient than xylene, and benzene is quite unsatisfactory for this purpose.

A few experiments are described wherein hydrazine salts are treated in turn with sodamide, calcium carbide and aluminum carbide. The latter two substances fail to react but sodamide reacts violently if undiluted. Hydrocarbons are unsatisfactory diluents for the purpose of preparing anhydrous hydrazine by this method.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

BENZOIN-ANIL-ANILIDE AND BENZOIN-PARA-TOLYL PARA-TOLUIDE AS AMMONO BENZOIN ACETALS

BY HAROLD H. STRAIN

RECEIVED AUGUST 22, 1928 PUBLISHED JANUARY 8, 1929

Introduction

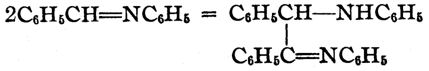
Upon carrying out a series of reactions to support the view that the Schiff's bases are aldehyde-acetals of an ammonia system of compounds, the writer found[1] that both benzylidene-aniline and benzylidene-*p*-toluidine undergo the benzoin condensation reaction, forming benzoin-anil-anilide and benzoin-p-tolyl-toluide, ammono compounds which are analogous to benzoin.[2]

---

[1] Strain, THIS JOURNAL, 50, **2218 (1928).**

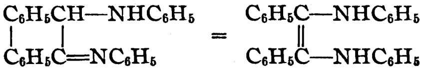
[2] For an explanation of the ammonia system of compounds cf. Franklin, ***Am. Chem.*** **J., 47, 285 (1912);** THIS JOURNAL, **46, 2137 (1924).**

This reaction, as well as the probable structure of these ammono benzoins, is illustrated by the following equation.



$$2C_6H_5CH{=}NC_6H_5 = \begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\ \ | \\ C_6H_5C{=}NC_6H_5 \end{array}$$

In addition to being analogous to the aquo benzoins, the ammono benzoins are also analogous to the aquo esters or acetals in that they have organic radicals attached to the nitrogen atoms. In this respect they resemble the ammono aldehyde acetals from which they are prepared and may therefore be regarded as ammono benzoin acetals. Furthermore, the ammono benzoin acetals may also be considered as substituted ammono glycolic aldehydes and should therefore exhibit the familiar enediol tautomerism characteristic of aquo glycolic aldehyde and other α-hydroxy aldehydes, as shown herewith.



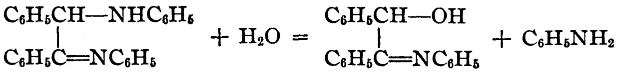
$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\ \ | \\ C_6H_5C{=}NC_6H_5 \end{array} = \begin{array}{l} C_6H_5C{-}NHC_6H_5 \\ \quad\ \ \| \\ C_6H_5C{-}NHC_6H_5 \end{array}$$

(keto form) (enediol form)

If the above analogies are real, then the ammono benzoins should undergo all of the reactions characteristic of aquo benzoin and aquo acetals. Upon hydrolysis they should form aquo benzoin and ammono alcohols, while upon ammonolysis they should form ammono benzoin and ammono alcohols. Nitridizing agents should convert them into ammono compounds analogous to the oxidation product of benzoin, that is, benzil. The ammono benzils thus formed should in turn be hydrolyzed to aquo benzil. The ammono benzoins should also be easily converted into indole derivatives, since they represent the intermediate compounds assumed to be formed when indole derivatives are prepared by the action of aniline hydrochloride on benzoin-anilide.[3]

As a matter of fact, all the foregoing predictions have been justified by the experimental work described in this paper.

Upon treatment with water, the ammono benzoins are partially hydrolyzed, forming aquo ammono benzoins and ammono alcohols. Thus benzoin-anil-anilide gives rise to benzoin-anilide and aniline



$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\ \ | \\ C_6H_5C{=}NC_6H_5 \end{array} + H_2O = \begin{array}{l} C_6H_5CH{-}OH \\ \quad\ \ | \\ C_6H_5C{=}NC_6H_5 \end{array} + C_6H_5NH_2$$

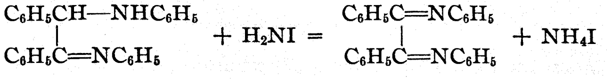
while benzoin-p-tolyl-p-toluide forms benzoin-p-toluide and *p*-toluidine.[4]

---

[3] Bischler and Fireman. Ber., 26, 1336 (1893).

[4] According to Voigt [(a) J. *prakt. Chem.*, (2) 31, 544 (1885), and (b) (2) 34, 2 (1886)] and (c) Japp and Murray [Ber., 26, 2638 (1893)] the structure of benzoin-anilide should be represented by Formula I, below. (d) Lachowicz [*Monatsh.*, 15, 402

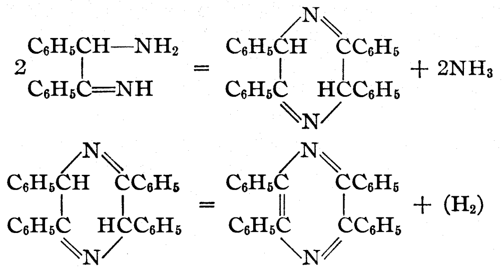
Nitridizing agents convert benzoin-anil-anilide into the corresponding ammono benzil, benzil-dianil, as illustrated by the following equation



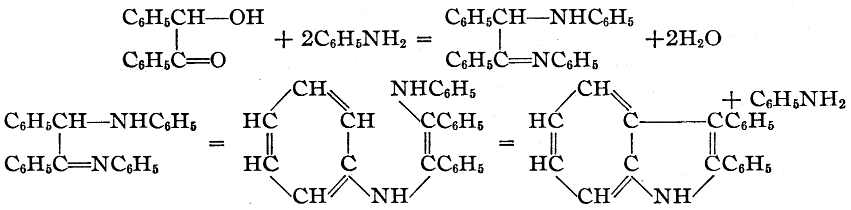
$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ | \\ C_6H_5C{=}NC_6H_5 \end{array} + H_2NI = \begin{array}{l} C_6H_5C{=}NC_6H_5 \\ | \\ C_6H_5C{=}NC_6H_5 \end{array} + NH_4I$$

while benzoin *p*-tolyl-*p*-toluide is nitridized to benzil-di-*p*-tolyl.

When ammonolyzed, the ammono benzoin acetals form tetraphenylpyrazine in rather poor yields. This reaction probably takes the course illustrated by the following equations, although no free hydrogen has been observed as a reaction product.

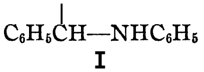


In studying the action of aniline upon benzoin at 200°, Lachowicz[4d] found that, in the presence of hydrogen chloride, benzoin and aniline reacted to form 2,3-diphenylindole.[3,4c,5] In order to explain the reaction Bischler and Fireman proposed the following mechanism, although they were unable to isolate the benzoin-anil-anilide as an intermediate product.



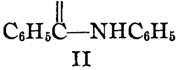
This mechanism has been verified by the writer by the conversion of the

(1894)], on the other hand, thinks that this compound has the structure represented by Formula III.



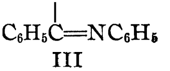
$$\begin{array}{l} C_6H_5C{=}O \\ | \\ C_6H_5CH{-}NHC_6H_5 \end{array}$$

I



$$\begin{array}{l} C_6H_5C{-}OH \\ \| \\ C_6H_5C{-}NHC_6H_5 \end{array}$$

II



$$\begin{array}{l} C_6H_5CH{-}OH \\ | \\ C_6H_5C{=}NC_6H_5 \end{array}$$

III

As a matter of fact, Formulas I and III are related to each other in a manner which may be shown by writing the transition compound, Formula II. Any one of the three formulas written above is derived from the other by the shift of a hydrogen atom analogous to that which takes place in the keto-enol isomerism of acetoacetic ester. However, no evidence is at hand to show that the stable form of the compound may be represented by any particular one of the above formulas.

[5] Japp and Murray, *J. Chem. Soc.*, 65,892 (1894).

ammono benzoins into the corresponding substituted indoles, as illustrated by the last reaction written above.

Experimental

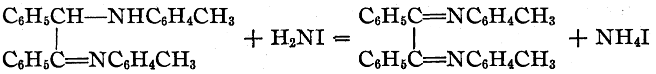
Hydrolysis of the Ammono Benzoins.—Benzoin-anil-anilide was hydrolyzed to the aquo ammono benzoin, benzoin-anilide, when boiled with 80% alcohol containing some hydrochloric acid. The benzoin-anilide obtained by this reaction melts at 99°. It was identical with benzoin-anilide prepared by the writer by the action of aniline on benzoin as described by Voigt,[4b] both compounds having the same crystalline form and the same solubility in alcohol, water and acids. A mixture of the two compounds melted at 99°.

Benzoin-*p*-tolyl-*p*-toluide was hydrolyzed by alcoholic hydrochloric acid to benzoin-*p*-toluide and *p*-toluidine. The mixed aquo ammono benzoin was found to be identical with that prepared by Voigt, both in melting point and solubility in acids and alcohol.[6]

Nitridation of the Ammono Benzoins.—Three-tenths g. of the ammono benzoin was dropped into a solution of 0.6 g. of iodine in liquid ammonia contained in a Faraday tube, which was then sealed and placed in an ice-bath until all of the iodine color had disappeared (about eight hours). At the end of this time, the deep yellow crystals of the benzoin-anil-anilide had completely dissolved, while light yellow crystals were found covering the walls of the tube. These crystals were washed several times and dried in a vacuum. They melted at 144°. The melting point given for benzil-dianil, prepared from benzil and aniline, by Lachowicz[7] is 142" and that by Siegfeld[8] is 141–142°. This difference in melting point must have been due to impurities contained in the previous preparations because both compounds had the same solubility in alcohol, water, ether and benzene. The writer repeated the work of Lachowicz and Siegfeld and found that it was impossible to obtain a compound which looked as pure as that obtained by the nitridation reaction. The melting point of the crystals thus prepared was 142°, but it was not changed when mixed with the crystals melting at 144°. Both compounds were hydrolyzed to benzoin and aniline as described by Lachowicz.

The writer also nitrized (oxidized) benzoin-anil-anilide to the ammono benzil by passing a current of air through a solution of the former in toluene or benzene. However, if the air is saturated with water vapor, a small quantity of benzanilide is formed, proving that the carbon to carbon bond is broken, a reaction which indicates that benzoin-anil-anilide may exist in the enediol form discussed above.

Benzoin-*p*-tolyl-*p*-toluide is only slowly nitridized by ammono hypo-iodous acid, due possibly to the slight solubility of this ammono benzoin in liquid ammonia. On the other hand, the reaction takes place very readily when carried out in benzene solution using air as the de-electronizing agent.



$$\begin{array}{l} C_6H_5CH—NHC_6H_4CH_3 \\ \;| \\ C_6H_5C{=}NC_6H_4CH_3 \end{array} + H_2NI = \begin{array}{l} C_6H_5C{=}NC_6H_4CH_3 \\ \;| \\ C_6H_5C{=}NC_6H_4CH_3 \end{array} + NH_4I$$

The benzil-di-*p*-tolyl obtained by the above reaction melted at 162° and was identical in every respect with that prepared by Lachowicz.[9]

Ammonolysis of the Ammono Benzoins.—Upon heating benzoin-anil-anilide or benzoin-*p*-tolyl-*p*-toluide with liquid ammonia in a sealed tube at 130° for ten hours, the ammono benzoins were found to dissolve while a few colorless, needle-shaped crys-

---

[6] Voigt, ref. 4 b, p. 15.

[7] Lachowicz, *Monatsh.*, 14, 283 (1893).

[8] Siegfeld, Ber., 25, 2601 (1892).

[9] Lachowicz, ref. 7, p. 289.

tals were formed. These crystals proved to be tetraphenylpyrazine. They dissolve in concentrated sulfuric acid, forming a deep red solution from which the pyrazine compound could be recrystallized upon dilution with water.

The melting point of the tetraphenylpyrazine obtained from the ammono benzoins was 252°, while that given by earlier investigators,[10] who used other methods of preparation, is 245–246°. The writer then repeated the work of Japp and Wilson and found that it was possible to prepare tetraphenylpyrazine by the action of ammonium acetate on benzoin, which melted at 252°. The crystals thus obtained showed no depression in melting point when mixed with those obtained by the ammonolysis reaction.

The liquid ammonia decanted from the crystals of tetraphenylpyrazine contained free aniline, or p-toluidine. No other pure compounds could be separated although the yield of tetraphenylpyrazine amounted to only a few per cent. of the weight of the ammono benzoins used in the reaction.

Formation of Substituted Indoles.—Benzoin-anil-anilide does not break down when heated to its boiling point. However, if it is dissolved in benzene or toluene which is saturated with dry hydrogen chloride and the resulting solution heated in a sealed tube for two hours at 180–200°, the reaction products are found to be 2,3-diphenylindole and aniline hydrochloride The latter is insoluble in the hydrogen chloride solution while the former is very soluble so that the two are easily separated. The yield is almost quantitative.

Benzoin-*p*-tolyl-*p*-toluide is converted into 2,3-diphenyl-5-methylindole and *p*-toluidine hydrochloride when heated with benzene and hydrogen chloride. One-half g. of the ammono benzoin formed 0.3 g. of the indole derivative and 0.13 g. of p-toluidine hydrochloride. The 2,3-diphenyl-5-methylindole melted at the recorded temperature and formed a chocolate brown picrate melting at 154°, as described by Bischler and Fireman.[11]

The experiments described in this paper were carried out under the direction of Dr. E. C. Franklin, to whom the writer is greatly indebted for the many helpful suggestions received during the course of the work.

Summary

Benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide are ammono benzoin acetals. As ammono acetals they can be ammonolyzed and hydrolyzed. As ammono benzoins they can be nitridized to ammono benzils.

The ammono benzoins are converted into indole derivatives by hydrogen chloride.

The structure of benzoin-anilide and the ammono benzoins has been discussed.

STANFORD UNIVERSITY, CALIFORNIA

---

[10] Leuckart, *J. prakt. Chem.*, [2] 41, 333 (1890); Japp and Wilson, *J. Chem. Soc.*, 49,826 (1886).

[11] Bischler and Fireman, ref. 3, p. 1342.

[COMMUNICATION NO. 367 FROM THE KODAK RESEARCH LABORATORIES]

THE ACTION OF FATTY ACIDS ON CELLULOSE[1]

BY C. J. MALM AND H. T. CLARKE

RECEIVED AUGUST 27, 1928 PUBLISHED JANUARY 8, 1929

When cellulose is heated with acetic acid, no obvious change in the external appearance of the fibers takes place, but esterification occurs and the resulting product contains combined acetyl. While an analogous action has been observed with anhydrous formic acid,[2] none appears to have been recorded in the cases of its homologs. We have found esterification to take place on boiling cellulose not only with acetic acid, but with the higher members of the series up to heptylic. The rates of esterification in these cases are lower than with acetic acid, apparently decreasing with rise in molecular weight.

The esterification of native cellulose fibers in this way tends to a limit expressed by the formula $C_{24}H_{39}O_{20}(COR)$, which in the case of acetic acid and propionic acid is reached after about one hundred hours of boiling under atmospheric pressure. The same result is reached in a shorter time by heating to a higher temperature, either under pressure or in the superheated vapor of the acid. On continuing the action for a prolonged time after this point is reached, esterification ceases, or occurs to only a very slight extent and very slowly (an effect which we incline to attribute to incipient decomposition of the cellulose under the drastic conditions of temperature). This approximate limit is observed with all forms of native cellulose and appears to be independent of the state of aggregation (indicated by the cuprammonium viscosity of the starting material).

When, on the other hand, the native cellulose is replaced by hydrated cellulose, such as rayon prepared from viscose, from cuprammonium solutions or by denitration of nitrocellulose, esterification tends toward a limit expressed by the formula $C_6H_9O_5(COR)$. The same is observed for mercerized cellulose and for cellulose obtained by saponification of precipitated cellulose acetate.

From these observations it must be concluded that, firstly, in native cellulose one hydroxyl group out of every twelve is chemically different from the rest, being capable of esterification without the intervention of acid anhydrides or of catalysts. The fact that one hydroxyl group out of twelve displays distinctive chemical properties is, in our opinion, an argument for regarding native cellulose as a multiple of the unit $C_{24}H_{40}O_{20}$.

---

[1] The results here described form the subjects of U. S. Patents 1,668,944 and 1,668,945 of 1928 and of pending applications.

[2] See E. C. Worden and L. Rutstein, *Kunststoffe*, 2, 325 (1912), for a summary of work on this subject.

Secondly, in hydrated cellulose four such hydroxyl groups are chemically different from the remaining eight.

The introduction of acyl groups to this limited extent causes no substantial alteration in the general appearance of the cellulose treated, beyond a tendency of the fibers to become weaker and more friable. Apart from the fact that they are hydrolyzed by alkali, the low esters are indistinguishable in chemical and physical properties from cellulose, being insoluble in organic liquids, but soluble in Schweitzer's reagent, in concentrated sulfuric or phosphoric acid, and in concentrated zinc chloride. The only marked difference which has been observed is concerned with the action of dyes, and is restricted to the more highly esterified products which are obtained from hydrated cellulose. Thus prolonged boiling with acetic acid confers upon rayon fibers the ability to retain basic dyes, such as Fuchsin and Malachite Green, which are quite inactive toward cellulose in its ordinary forms.

Investigation of saponified cellulose acetates indicates that fibers regenerated (by saponification) from cellulose which has been acetylated heterogeneously yield, on boiling with acetic acid, a series of esters, the limiting composition of which appears to be considerably lower in acetyl than that of those obtained from cellulose regenerated from acetates which have been produced in solution. This difference in chemical behavior is in harmony with the observation of Herzog[3] that the same two types of regenerated cellulose differ in their Roentgen spectra, which correspond, respectively, to that of native cellulose and that of hydrated cellulose. Owing, no doubt, to partial hydration of the cellulose during the heterogeneous acetylation, the fibers regenerated from the acetate so prepared take up higher proportions of acetyl than do the fibers of pure native cellulose, but the amounts are much lower than with cellulose regenerated from acetate which has been in solution.

Experimental

The general procedure adopted in the boiling experiments was as follows: the air-dried cellulose was immersed in 20 to 30 times its weight of glacial acetic acid in a round-bottomed pyrex flask, and gently boiled on an air-bath under reflux. The upper end of the condenser was fitted with a calcium chloride tube to prevent the access of atmospheric moisture. After a few hours of boiling, the heating was discontinued and as much of the acid as possible drained from the cellulose in order to remove soluble impurities as well as moisture originally present and formed by reaction. Fresh acid was added and boiling continued. Samples were periodically removed, thoroughly washed with distilled water and dried for analysis.

When operating with the higher acids, the reflux condenser was replaced by a fractionating column by means of which the water could be removed from the mixture. This system was also occasionally applied to the case of acetic acid.

For analysis, 1-g. samples were suspended in 20 cc. of 75% ethyl alcohol and warmed

---

[3] R. O. Herzog, Ber., 60,600 (1927).

for half an hour at 50–60°, then treated with 20.0 cc. of 0.5 *N* aqueous sodium hydroxide. After holding at 50–55° for fifteen minutes, the mixture was allowed to stand, well stoppered, for forty-eight hours at room temperature. The excess alkali was then titrated with 0.5 *N* acid, using phenolphthalein. It was found possible, in the case of the acetic esters, to reduce the time to twenty-four hours, but for the esters of higher acids the full forty-eight hours were found necessary.

The following experiments are typical of a very large number.

Surgical Cotton (High Viscosity) Boiled with Acetic Acid

Time, hours	0	1	2	4	8	16	24	48	72	96
Acetyl, %	0.6	0.8	1.3	2.4	2.9	3.7	4.5	5.5	6.0	6.2

The formula $C_{24}H_{39}O_{20}(COCH_3)$ requires $CH_3CO = 6.2\%$.

Surgical Cotton Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	4.6	5.5	6.0	6.6	6.5	6.8	6.4

At the end of 500 hours, the cotton had become considerably disintegrated.

Linters (Medium Viscosity) Boiled with Acetic Acid

Time, hours	24	48	96	144	200	300
Acetyl, %	4.0	4.9	5.1	5.5	6.2	6.4

Linters (Low Viscosity) Boiled with Acetic Acid

Time, hours	24	48	96	200	300
Acetyl, %	4.4	5.0	5.6	6.9	6.8

Commercial Sulfite Pulp Boiled with Acetic Acid

Time, hours	24	48	96	200	300
Acetyl, %	5.1	5.6	6.7	7.6	7.5

This sample of sulfite pulp contained about 90% of a-cellulose and some colored impurities soluble in hot acetic acid.

Surgical Cotton Boiled with Propionic Acid

Time, hours	24	48	96	160	200
Propionyl, %	4.7	5.7	6.4	7.9	8.0

The cotton had become badly degraded after 200 hours. The formula $C_{24}H_{39}O_{20}(COC_2H_5)$ requires $C_2H_5CO = 8.1\%$.

Linters (Medium Viscosity) Boiled with Propionic Acid

Time, hours	24	48	96	144	200
Propionyl, %	6.7	7.4	7.8	8.0	8.2

Linters (Medium Viscosity) Boiled with n-Butyric Acid

Time, hours	24	48	96	144	200
Butyryl, %	5.0	5.9	8.6	10.2	10.9

The formula $C_{24}H_{39}O_{20}(COC_3H_7)$ requires $C_3H_7CO = 9.9\%$.

Surgical cotton was also heated with acetic acid in sealed glass tubes to 140–145°.

Time, hours	8	16	24	48
Acetyl, %	4.6	5.7	7.4	7.5

The last two samples were somewhat degraded.

Surgical cotton was heated to 150–155° in a current of acetic acid vapor.

Time, hours	6	7	20
Acetyl, %	3.8	4.0	6.0

In the following four experiments, commercial samples of artificial silk, prepared by different processes, were employed. They show very clearly that the acetyl content tends to a limit not far removed from the 21.1% required by the formula $C_6H_9O_5(COCH_3)$.

Viscose Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	10.2	11.6	14.5	20.0	21.2	22.2	22.3

Cuprammonium Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600	700
Acetyl, %	8.2	10.8	14.6	19.0	20.9	22.0	22.2	22.4	22.1

Denitrated Nitrocellulose Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	9.1	11.0	13.2	18.5	20.6	21.6	22.0

The same effect is found with cellulose after mercerization. Surgical cotton was soaked for twenty-four hours at 20° in 18% and in 40% sodium hydroxide solution, well washed with water, finally with acetic acid and boiled with acetic acid.

Cellulose Mercerized with 18% NaOH Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600
Acetyl, %	9.3	11.6	13.5	17.5	19.2	20.9	21.6	21.9

Cellulose Mercerized with 40% NaOH Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600
Acetyl, %	10.2	13.0	14.8	17.6	19.5	22.2	22.6	22.6

A sample of surgical cotton, mercerized with 18% sodium hydroxide for twenty-four hours at 20°, was heated to 150–155' in a current of acetic acid vapor.

Time, hours	6	12
Acetyl, %	6.7	9.5

Cellulose acetate was prepared by a standard method, using acetic anhydride and a mineral acid catalyst in acetic acid. The resulting solution **was** poured into water and the amorphous precipitate thoroughly washed. It contained 44.5% of acetyl. It was then completely saponified by the process (described above) for the determination of acetyl, well washed with water and finally with acetic acid, and boiled with acetic acid.

Time, hours	0	24	48	96	200	300	400	500
Acetyl, %	0.0	10.0	12.0	14.2	17.8	20.2	22.3	22.2

Surgical cotton was acetylated by a standard method employing acetic anhydride and a mineral catalyst in carbon tetrachloride. The resulting product, which preserved the original fibrous structure of the cotton, contained 43.6% of acetyl. It was completely saponified by the same method as above, well washed with water and finally with acetic acid, and boiled with acetic acid.

Time, hours	24	48	96	200
Acetyl, %	6.7	7.6	9.8	10.8

After 300 hours of boiling, the fibers had become completely disintegrated.

Acknowledgment is due to T. F. Murray, Jr., and A. W. Crane for carrying out the analytical work.

Summary

1. Native cellulose is esterified on heating with acetic acid, the reaction coming to an end when the resulting product contains 6–7% of acetyl. This corresponds to the composition $C_{24}H_{39}O_{20}(COCH_3)$. An analogous effect is produced with propionic acid and butyric acid.

2. Hydrated cellulose, prepared by regeneration of cellulose from its nitrate, from viscose, from its solution in Schweitzer's reagent or from dissolved cellulose acetate, yields, on heating with acetic acid, esters having a limiting composition expressed by the formula $C_6H_9O_5(COCH_3)$.

3. Mercerized cellulose behaves in the same way as hydrated cellulose.

4. Cellulose regenerated from cellulose acetate which has preserved its original fibrous structure behaves, in this reaction, more like native cellulose than hydrated cellulose.

5. In view of the definite limit of esterifiability of native cellulose by acids alone, it is concluded that the constitution of cellulose must be expressed as a multiple of the unit $C_{24}H_{40}O_{20}$.

ROCHESTER, NEW YORK

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE RELATIONSHIP OF THE CONSTITUTION OF CERTAIN ALKYL HALIDES TO THE FORMATION OF NITROPARAFFINS AND ALKYL NITRITES

BY ROBERT B. REYNOLDS AND HOMER ADKINS

RECEIVED AUGUST 30. 1928 PUBLISHED JANUARY 8, 1929

The reaction of alkyl halides with metallic nitrites results in the formation of varying proportions of the isomeric nitroparaffins and alkyl nitrites. It has been shown by various investigators that the ratio of the isomers in the reaction mixture is dependent upon the nature of the particular alkyl radical and metal used.[1]

Despite the very considerable interest in the subject, as shown by the list of publications, there has been no systematic or accurate determination of the proportions of isomers produced in the reaction of any extensive list of reagents. A summary of the previous observations made upon the reactions of various alkyl halides with silver nitrite is given in Table I.

TABLE I

FORMATION OF ALKYL NITRITES AND NITROPARAFFINS FROM VARIOUS ALKYL HALIDES WITH SILVER NITRITE

Alkyl halides	Yield of isomers, %	Nitroparaffin, %	Alkyl nitrite, %	Observers
Methyl iodide	?	90	None	Meyer and Stuber
Methyl iodide	63	52.6	47.4	Ray and Neogi
Ethyl iodide	?	"50"	"50"	Meyer and Stuber
Ethyl iodide	83	52.9	47.1	Ray and Neogi
n-Propyl iodide	?	Mainly	?	Meyer and Rilliet
*Iso*propyl iodide	80.7	44.1	55.9	Ray and Neogi
Allyl iodide	Poor	?	?	Meyer and Chojnacki
Allyl bromide	34	Mostly	Small	Schiff
Allyl bromide	?	Mostly	Small	Brackebusch
n-Butyl iodide	?	53	?	Züblin
Isobutyl iodide	?	"50"	"50"	Demole
Sec.-butyl iodide	58	?	?	Meyer and Locher
Tert.-butyl iodide	?	Small	Mainly	Tscherniak
Iso-amyl iodide	34.7	79.5	20.5	Ray and Neogi

The present investigation was undertaken in order to ascertain the facts with regard to the proportion of isomers formed from various alkyl halides and silver nitrite, in the hope that ultimately some light would

---

[1] (a) V. Meyer, Stuber, Rilliet and Chojnacki, Ann., **171**, 1 (1872); (b) V. Meyer and Locher, *ibid.*, **180**, 134 (1876); (c) V. Meyer and Stuber, *Ber.*, **5**, 203, 399 (1872); (d) V. Meyer and Rilliet, *ibid.*, **5**, 1032 (1872); (e) V. Meyer and Chojnacki, *ibid.*, **5**, 1037 (1872); (f) Tscherniak, Ann., **180**, 155 (1876); (g) Ray and Neogi, *Proc. Chem. Soc.*, 23, 246 (1907); (h) Demole, Ann., **175**, 142 (1874); (i) Eichler, *Ber.*, **12**, 1883 (1879); (j) Brackebusch, *ibid.*, **7**, 225 (1874); (k) Schiff, *ibid.*, **7**, 1141 (1874); (l) Züblin, *ibid.*, 10, 2083 (1877).

be shed upon the relationship between the constitution of the reactants and the relative rates of the simultaneous reactions.

Preparation of **Alkyl Halides.**—*n*-Propyl, isopropyl, n-butyl and *iso*butyl iodides were prepared through the reaction of the corresponding alcohol with a mixture of red and white phosphorus and iodine as described by Adams, Kamm and Marvel.[2] It was found that a better product was obtained in the case of *sec.*-butyl iodide if the older method of adding iodine to red phosphorus contained in the alcohol was used. The method of Norris[3] was used for the preparation of *tert.*-butyl iodide and that of Freunder and Damond[4] for the preparation of cyclohexyl iodide. The sodium bromide method[5] was used for the preparation of n-propyl and n-butyl bromide. The method of Norris[6] was used for the preparation of *sec.*-propyl bromide. *Iso*butyl, *sec.*-butyl, *tert.*-butyl, iso-amyl, n-heptyl and *sec.*-octyl bromides were prepared through the reaction of the corresponding alcohol with phosphorus tribromide. The latter was prepared by the method of Schorlemmer.[7] In the preparation of the alkyl halide the tribromide was allowed to drop slowly into the alcohol held in an ice-bath. The reaction mixture was allowed to stand for an hour or so after the addition of the last of the tribromide and then gently warmed. The halide was then separated, washed with water (then with sulfuric acid in the case of isobutyl bromide) then with a 10% solution of sodium carbonate and repeatedly with water. The product was dried over calcium chloride and fractionated. The yields were from 80 to 85% of the theoretical. Benzyl bromide was prepared through the reaction of the alcohol with constant boiling hydrobromic acid in the molecular ratio of 1:3. The yield was 92%. Allyl and β-phenylethyl bromide were obtained from the Eastman Kodak Company.

Reaction of **Silver Nitrite with Various Alkyl Halides.**—The reaction of an alkyl halide with silver nitrite was in general carried out as by Victor Meyer except that the silver nitrite was not mixed with sand. The desired amount of silver nitrite was placed in a round-bottomed flask which was connected by a ground-glass joint to a dropping funnel and a spiral condenser. The alkyl halide was then slowly dropped onto the nitrite, the flask being cooled in an ice–salt mixture. If the reaction was too rapid, more or less decomposition took place with the evolution of oxides of nitrogen. The reaction mixture was allowed to stand for two or three hours in the ice-bath after the addition of the last of the alkyl halide. The mixture was then gently refluxed in a water or oil-bath for four or five hours. The mixture of alkyl nitrite and nitroparaffin was removed from the reaction mixture by distillation, first at atmospheric and then under reduced pressure. If the distillate showed a test for a halide (as it usually did), the mixture was refluxed with a further quantity of silver nitrite. The distillate from this second treatment with silver nitrite was analyzed for nitrogen by the Dumas method. If the result of this analysis indicated that the distillate was a pure mixture of the isomeric alkyl nitrite and nitroparaffin, the mixture was analyzed as described below for the percentage of nitroparaffin.

In the case of one of each of the two preparations from n-butyl iodide, n-propyl and n-heptyl bromide, the method was changed in that the silver nitrite was slowly added

---

[2] Adams, Kamm and Marvel, "Organic Chemical Reagents," University of Illinois Bulletin, Urbana, 1919, Vol. I, p. 19.

[3] Norris, Am. *Chem.* J., 38, 641 (1907).

[4] Freunder and Damond, *Compt.* rend., 141, 593 (1905).

[5] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1, 6 (1921).

[6] Norris, ref. 3, p. 640.

[7] Roscoe and Schorlemmer, "Treatise on Chemistry," Macmillan Co., New York, 1920, Vol. I, 5th ed., p. 649.

(two to three hours) with shaking to the alkyl halide. This modification in the procedure had no effect upon the yield or proportion of the isomers formed. This procedure was used in both of the preparations for *sec.*-octyl bromide, *tert.*-butyl bromide and allyl bromide. In the case of the first of these the reaction mixture was not refluxed but merely heated to 120–125° for two or three hours. *Tert.*-butyl bromide at first reacted rather slowly with silver nitrite but after a little had reacted the reaction became so vigorous that ten hours was consumed in adding 60 g. of silver nitrite. Allyl bromide was so reactive that it was necessary to add the 35 g. of silver nitrite in very small portions during an interval of twenty hours.

The distillates from the reactions of *tert.*-butyl iodide and cyclohexyl iodide with silver nitrite represented yields of less than 50% of the theoretical amount. The determination of nitrogen showed that these distillates were very far from being a mixture of only the nitro compound and the nitrite. Rather considerable amounts of benzaldehyde were formed in the reaction of benzyl and β-phenylethyl bromides. Attempts to purify the mixture of isomers from the benzaldehyde were unsuccessful. The reaction products of these four alkyl halides therefore were not analyzed for nitroparaffins.

Analysis of Reaction Mixtures.—All previous investigators have attempted to determine the proportion of the isomers in the reaction product by fractional distillation, but in this case a more accurate method was desired. Various methods were rather thoroughly examined and discarded for one reason or another before an accurate but laborious method of analysis was adopted. Attempts were made to saponify the ester and determine the nitrous acid through its reaction with urea to form carbon dioxide and nitrogen. Attempts were also made to titrate the nitrous acid in the presence of the nitroparaffin. Attempts also were made to determine the nitrous acid iodometrically, but all of these methods failed to give accurate results when used for the analysis of mixtures.

The method finally adopted for the analysis involved the addition of an *alcoholic* solution of sodium hydroxide to a weighed sample of a mixture of isomers. The salt of the nitro compound was thereby formed and the alkyl nitrite saponified. The solution was then evaporated and the residue, consisting of the sodium salt of the nitro compound and sodium nitrite,[8] analyzed by a wet combustion method for carbon. From these data it is possible to calculate the percentage of nitro compound in the mixture of isomers.

The apparatus used for the analysis was arranged as follows. [illegible] supply of pure oxygen was led into the top of a 125-cc. dropping funnel whose stem passed through a ground-glass joint to the bottom of a 300-cc. Kjeldahl type of flask. A tube led from the top of this flask through a spiral condenser to a U-tube filled with pumice and chromic anhydride. The products of combustion then passed through two U-tubes containing glass wool plugs saturated with anhydrous sulfuric acid and a layer of acid partially filling the space at the bottom of the U. The gases then passed into a combustion tube supported in a gas furnace. Copper oxide was placed for a length of 5 inches in

---

[8] White and Holben, *Ind.* Eng. *Chem.*, **17**, 83 (1925); Desgrez and Venario, *Compt. rend.*, **180**, 886 (1925).

the center of the tube, while reduced copper spirals were placed on each side. After leaving the combustion furnace, the gases passed through two sulfuric acid drying tubes and then into a Geissler potash bulb properly provided with guard tubes containing soda lime and calcium chloride.

The procedure for the analysis of the mixture of isomers was as follows. A sample of from 0.15 to 0.5 g. was weighed into previously weighed, thin-walled glass vials and immediately sealed off. The vial was placed in the combustion flask and 10 cc. of a 0.1 *N* alcoholic solution of carbonate-free sodium hydroxide added. (The latter was prepared from absolute alcohol and sodium hydroxide.) The vial was broken and the mixture allowed to stand for a few minutes. The volatile material was then removed by distillation from a bath, first at atmospheric pressure until all the visible liquid had distilled, and then under a pressure of a few millimeters. It was found necessary to take great care at this point in order to prevent spattering. The temperature was finally raised to 135–140° during three or four hours. In the case of the heptyl and octyl compounds the temperature was raised to 180° for an hour or two and then maintained at 155° overnight.

After the volatile material was thus expelled, the combustion flask was attached to the rest of the combustion apparatus. Ten to 15 cc. of a chromic acid solution (100 g. of chromic anhydride in 200 cc. of water) was then added under a slight pressure of oxygen followed by 100 cc. of sulfuric acid which had been previously boiled for two hours. Fifteen to 20 cc. of the acid was allowed to remain in the dropping funnel during the combustion. The combustion flask was slowly heated with a Bunsen burner so that there was a steady flow of gas into the potash bulb. Finally the oxidation mixture was boiled for a few minutes. After the flask had cooled somewhat, the system was swept out with a slow stream of purified oxygen. A correction was applied of 0.0327 g. of carbon dioxide.

That the method gives reasonably accurate results is shown by the results of analyses carried out on pure nitrobutane and mixtures of it with n-butyl nitrite. Representative analyses are given in Table II.

TABLE II

ANALYSES FOR NITROBUTANE IN MIXTURES WITH *n*-BUTYL NITRITE

$C_4H_9NO_2$, present, g.	C_4H_9ONO, present, g.	$C_4H_9NO_2$, found, g.	$C_4H_9NO_2$, present, %	$C_4H_9NO_2$, found, %
0.4855	None	0.4834	100	99.57
.1147	None	.1140	100	99.39
.4475	None	.4480	100	100.11
.1201	None	.1195	100	99.40
.1683	None	.1665	100	99.75
.1722	0.6370	.1778	21.28	21.96
.1768	1.3543	.1752	11.54	11.42
.2181	1.2920	.2242	14.44	14.84
.2467	0.2107	.2452	53.98	53.60

The method of analysis just described is not applicable to those nitro compounds in which the nitro group is attached to a tertiary carbon atom. The only compound of this type investigated was 2-nitro-isobutane. Mixtures of this compound with *tert.*-butyl nitrite were analyzed in two ways. The amount of the ester present was determined by hydrolyzing the mixture in the presence of standard acid and also by saponifying in a standard solution of sodium hydroxide. The average of three determinations by each method agreed to within less than a tenth of a per cent. The percentage of nitro compound was calculated by difference.

A summary of the data obtained in this investigation of the iodides and bromides is given in Tables III and IV. The name of the alkyl halide undergoing reaction with silver nitrite is given in Col. 1 of Table III, the boiling range of the alkyl halide in Col. 2 and the weight of alkyl halide used in each preparation in Col. 3. The weight of silver nitrite used is given in Col. 4. In Col. 5 are given the boiling-point ranges of the mixture of isomers. The weights of the mixture of isomers are given in Col. 6 for each of two preparations. The percentages of nitrogen found by Dumas determinations in the mixture of isomers are given in Cols. 7 and 8. The percentages of nitrogen theoretically present in the nitrite and nitro compound concerned are given in Col. 9.

TABLE III
DATA FOR VARIOUS PREPARATIONS OF MIXTURES OF ALKYL NITRITES AND NITROPARAFFINS

Alkyl halide			$AgNO_3$,	Yield				
Name	B. p., °C.	G.	g.	B. p., °C.	G.	N, found, %		Calcd., %
n-Propyl	102–102.5	50	60 + 15	56–132	22.0	16.16	16.6	15.70
iodide	102–102.5	50	60 + 15	56–132	23.5	15.55	15.41	15.70
Sec.-propyl	89–89.5	50	60 + 15	44–120	19.0	15.30	15.35	15.70
iodide	89–89.5	50	60 + 15	44–120	18.6	15.15	...	15.70
n-Butyl	126.5–127	50	50 + 15	74–152	23.8	13.92	13.45	13.59
iodide	126.5–127	50	50 + 15	74–152	24.5	13.37	13.15	13.59
Isobutyl	120–120.5	50	50 + 15	66–139	21.2	13.25	13.35	13.59
iodide	120–120.5	50	50 + 15	66–139	20.8	13.40	13.32	13.59
Sec.-butyl	116.2–117.3	50	50 + 15	67–140	19.8	13.22	13.42	13.59
iodide	116.2–117.3	50	50 + 15	67–140	19.5	13.52	...	13.59
n-Propyl	69.5–71	40	50 + 15	56–132	24.8	15.62	...	15.70
bromide	69.5–71	40	50 + 15	56–132	25.3	15.45	...	15.70
Sec.-propyl	58–59.2	40	50 + 15	44–120	23.0	15.15	15.50	15.70
bromide	58–59.2	40	50 + 15	44–120	22.6	15.46	15.15	15.70
n-Butyl	100–102	50	60 + 15	74–152	33.3	13.65	13.40	13.59
bromide	100–102	50	60 + 15	74–152	32.9	13.65	...	13.59
*Iso*butyl	89.5–91	50	60 + 15	66–139	29.3	13.35	13.38	13.59
bromide	89.5–91	50	60 + 15	66–139	28.7	13.25	...	13.59
Sec.-butyl	90–91.2	45	55 + 15	67–140	23.2	13.25	13.48	13.59
bromide	90-91.2	45	55 + 15	67–140	23.0	13.15	...	13.59
Tert.-butyl	72–73.1	50	60 + 15	62–127	22.5	13.15	...	13.59
bromide	72–73.1	50	60 + 15	62–127	...	...	...	...
Iso-amyl	120–121	50	55 + 15	98–160	30.0	11.75	...	11.95
bromide	120–121	50	55 + 15	98–160	30.4	11.65	...	11.95
n-Heptyl	177–178.5	50	50 + 15	154–196	38.5	9.54	9.57	9.64
bromide	177–178.5	50	50 + 15	154–196	38.0	9.47	...	9.64
Sec.-octyl	71 (14 mm.)	50	45 + 15	164–213	35.5	8.51	8.40	8.80
bromide	71 (14 mm.)	50	45 + 15	164–213	34.2	8.58	8.45	8.80
Allyl	69–71	25	35 + 10	43–130	15.2	15.85	...	16.08
bromide	69–71	21.5	30 + 10	43–130	13.2	15.70	...	16.08

TABLE IV

YIELDS OF NITROPARAFFIN AND ALKYL NITRITES

Alkyl radical	Iodides Mixed isomers isolated, %	 Nitro compound in mixture. %	Bromides Mixed isomers isolated, %	 Nitro compound in mixture, %
Allyl	..	..	74.0	79.8
n-Propyl	85.9	66.9	86.1	77.4
Sec.-propyl	71.7	31.8	78.5	40.3
n-Butyl	85.1	60.7	88.2	77.9
*Iso*butyl	74.9	40.0	77.2	57.8
Sec.-Butyl	70.0	31.9	68.3	30.0
Tert.-butyl	..	..	60.0	48.3
Iso-amyl	..	..	78.2	67.5
n-Heptyl	..	..	94.3	71.0
Sec.-octyl	..	..	82.1	34.3

From three to five combustions were carried out on samples of each of the two preparations for each of the alkyl halides. Combustions on the same preparation never varied more than 1.7% from the average and in the great majority of cases the variation was not more than 0.5%. Combustions on different preparations never varied more than 1.1% from the average and rarely more than 0.7%. The averages of all these data are given in Table IV along with the average (two or more preparations) yield of mixed isomers.

n-Butyl chloride apparently does not react at its boiling point with silver nitrite as do the bromide and iodide. Iso-amyl chloride reacted but not at all completely when it was refluxed with silver nitrite. When 25 g. was heated with 45 g. of silver nitrite in a sealed tube at the boiling point of toluene for twenty-four hours, the product, weighing 22 g., contained 10.1% of chlorine calculated as iso-amyl chloride. The percentage of nitrogen in a mixture of the isomers with this percentage of the alkyl halide would be 10.77%. Actually 10.47 and 10.62% of nitrogen was found by analysis by the Dumas method. The analysis of the mixture showed that the isomers were present in the ratio of 30.1% of the nitro-*iso*pentane to 69.9% of the iso-amyl nitrite. The yield of the mixture of isomers was calculated to be 81.1% of the theoretical after allowance had been made for the unreacted *iso*-amyl chloride. Attempts to secure complete reaction of the iso-amyl chloride were unsuccessful.

Discussion of Results

The experimental results may be considered from several points of view.

I. A Comparison of Alkyl Iodides and Bromides as to the Amounts and the Proportions of Nitro Compound and Nitrite Formed.—A larger percentage of nitro compound was produced from the alkyl bromides than from the alkyl iodides, except in the case of *sec.*-butyl bromide. The percentage of 2-nitrobutane formed from *sec.*-butyl bromide was 1.3% less than that formed from *sec.*-butyl iodide.

The yields of mixtures isolated were from 10 to 17% higher with the bromides than with the iodides, except in the case of *sec.*-butyl bromide. *Sec.*-butyl iodide gave 1.7% higher yields than did *sec.*-butyl bromide.

II. The Relation of the Branching of the Chain as to the Proportion of the Isomers Formed.—The primary halides containing a branched chain did not give as high a proportion of nitro compound as did the straight chain compounds. For example, isobutyl bromide gave 57.9% of the nitro compound while n-butyl bromide gave 77.9% of nitro compound. The effect of the *iso* grouping in lowering the proportion of nitro compound apparently becomes less pronounced as it is further removed from the halogen. Isopentyl bromide gave 67.5% of the nitro compound, a proportion which approaches, although it is distinctly lower than, that for a straight chain bromide.

III. The Relation of the Position of the Halogen to the Proportion of the Isomers Found.—If the halogen in the alkyl halide is on a *sec.*-carbon atom, the proportion of nitro compounds is materially less than it is for the corresponding primary alkyl halide. In the case of the propyl and butyl compounds the proportion of the nitro compounds from the *sec.*-halides is in the vicinity of one-half the percentages in the case of the primary halides. It was rather surprising to find that with a branched chain and with the halogen on a *tert.*-carbon atom the proportion of nitro compound was higher than it was for the corresponding *sec.*-halide. *Tert.*-butyl bromide showed 48.3% of nitro compound as contrasted with 30% for the *sec.*-butyl and 57.9% for the isobutyl. Sidgwick states that tertiary halides gave almost entirely the nitrite and very little of the nitro compound. Tscherniak found that by the interaction of *tert.*-butyl iodide and silver nitrite, very little 2-nitro-isobutane was formed, but a larger percentage of the *tert.*-butyl nitrite was formed, no figures being reported.

IV. The Effect of Lengthening the Chain as to Proportion of the Isomers Formed.—It cannot be stated that there was in general either an increase or a decrease in proportions of nitro compound with increasing molecular weight of the alkyl group. n-Butyl iodide gave 5% lower than n-propyl iodide while n-butyl bromide gave 0.5% higher than the n-propyl bromide. n-Heptyl bromide gave only 6% less than the butyl compound. In the case of the iodides there was no difference between *sec.*-propyl and *sec.*-butyl, while in the case of bromides the percentage of nitro compounds dropped from 40.3 to 30%. Going higher in the secondary series to *sec.*-octyl, there is a slight increase in the proportion of nitro compound. As has been noted above in the case of the iso-compounds, there was a considerable increase in the proportion of nitro compound with increasing molecular weight. Sidgwick[9] states that all halides con-

---

[9] Sidgwick, "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1910, p. 140.

taining more than 4 carbon atoms give very low yields of the nitro compound.

V. The Effect of **Unsaturation** as to Proportion of the Isomers Formed.—The porportion of nitro compound formed from allyl bromide as compared with that of n-propyl bromide indicates that unsaturation has little or no effect on the relative proportions of nitro compound and alkyl nitrite formed.

VI. Relation between Constitution of the **Alkyl** Halide and Yield **of** the Mixture of Isomers.--The highest yields of the mixed isomers were isolated from the reaction of normal alkyl halides, the yield increasing with lengthening of chain in the case of alkyl bromides. *n*-Butyl iodide gave an 0.8% lower yield than did n-propyl iodide. With the exception of the *sec.*-butyl halides, the *sec.*-alkyl halides gave better yields than did the iso-alkyl halides. *Sec.*-butyl iodide gave a 70% yield and the corresponding bromide a 68.3% yield, while *sec.*-octyl bromide gave an 82% yield. *Sec.*-propyl iodide and isobutyl bromide gave an 82% yield. *Sec.*-propyl iodide and isobutyl iodide gave 71.8 and 74.9% yields, respectively, while the corresponding bromides gave 78.5 and 77.3% yields, respectively. Allyl bromide gave a yield of 74%. A yield of only 60% was obtained from *tert.*-butyl bromide.

VII. Relation between Constitution of **Alkyl** Halides and Rapidity of Reaction.—The reaction was more rapid with the branched chain alkyl halides and with the secondary halides than it was with the straight chain. normal alkyl halides. *Tert.*-butyl bromide was the most active of all the saturated alkyl bromides used. The secondary alkyl bromides were more active than the corresponding iso-alkyl halides. Allyl bromide was the most active of all the bromides used. The alkyl iodides react much more rapidly than do alkyl bromides, but the relative reactivities of the various iodides were about the same as with the bromides.

WI. A Comparison of **iso-Amyl** Chloride and Bromide.—The proportion of nitro compound was much less in the case of the reaction of *iso*-amyl chloride than it was for *iso*-amyl bromide. The chloride reacts less rapidly but the yield of the mixture of isomers is about the same as for the bromide.

IX. Mechanism of Reaction.—There seems to have been no adequate hypothesis advanced to account for the differences in the ratio of alkyl nitrites and nitroparaffin produced by the reaction of different alkyl iodides.[10] (Apparently it has not been previously realized that the nature of the halogen also played an important role in determining the proportion of the

---

[10] (a) E. Reynolds, J Chem. *Soc.*, *83*, 643 (1903); (b) Ray and Ganguli, *Proc. Chem. Soc.*, 21, 278 (1905); (c) Diners, *ibid.*, 21, 281 (1905); (d) Ray and Neogi, *J.* Chem. *Soc.*, 89, 1905 (1906); (e) Neogi, *ibid.*, 105,2371 (1914); (f) Neogi and Chowdhuri, *ibid.*, 109, 701 (1916).

isomers formed.) It seems probable to the authors that the two reactants form an addition compound, as suggested by Nef for the cyanides and isocyanides, although it may well be questioned whether a molecular compound is not formed instead of definite primary valences being set up as postulated by Nef. Each component of this molecular compound, alkyl group, metal and halogen, would then exert its influence in determining the relative rates of the two modes of decomposition whereby nitroparaffin and alkyl nitrite are formed.[11] This hypothesis is vague; it explains nothing and predicts nothing, yet it seems that at least for the present it is not possible to advance a more specific one without going far beyond experimental justification.

Summary

A quantitative study has been made of the amount and proportion of isomeric nitroparaffins and alkyl nitrites simultaneously formed through the reaction of silver nitrite and the following list of alkyl halides: n-propyl, isopropyl, n-butyl, isobutyl and *sec.*-butyl iodides, and n-propyl, isopropyl, n-butyl, isobutyl, *sec.*-butyl, *tert.*-butyl, iso-amyl, n-heptyl, *sec.*-octyl and allyl bromides and iso-amyl chloride.

It was found that a larger proportion of nitro compound was produced from the bromides than from the iodides except in the case of *sec.*-butyl bromide. Iso-amyl bromide gave over twice as large a percentage of the nitro compound as did the iso-amyl chloride. The yield of the isomers isolated was from 10 to 17% higher from the bromides than from the iodides, except in the case of *sec.*-butyl bromide. Primary halides containing a branched chain did not give as high a proportion of nitro compound as did the straight chain compounds. If the halogen in the alkyl halide is on a secondary carbon atom, the amount of formation of the nitro compound is materially less than it is for the corresponding primary or tertiary alkyl halide. It cannot be said that there is in general either an increase or a decrease in proportion of nitro compounds with increasing molecular weight of the alkyl group. The results obtained with allyl bromide indicate that unsaturation has little or no effect on the ratio of isomers formed. The highest yields of the mixed isomers were isolated from the reaction of normal alkyl halides, the yield increasing with lengthening of the chain in the case of the bromides. The order of increasing reactivity of the alkyl halides is allyl, *tert.*-butyl, *sec.*-halides, *iso*-alkyl, and n-alkyls. The iodides are more reactive than the bromides.

Attempts to prepare mixtures of the isomers sufficiently pure for analysis were unsuccessful when *tert.*-butyl iodide, cyclohexyl iodide, benzyl bromide or 2-phenylethyl bromide was used.

MADISON, WISCONSIN

---

[11] Cf. Falk, "Chemical Reactions, Their Theory and Mechanism," Chemical Catalog Co., New York, 1920.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND CO., No. 45]

THE IDENTIFICATION OF ALKYLBARBITURIC ACIDS

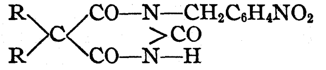
BY EDWARD LYONS AND ARTHUR W. DOX

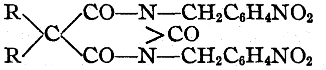
RECEIVED AUGUST 30, 1928 PUBLISHED JANUARY 8, 1929

The use of *p*-nitrobenzyl bromide as a reagent for the identification of acids was proposed by Reid.[1] Nearly one hundred acids were tested of which about 90 gave solid esters melting at convenient temperatures. Although Reid had in mind the carboxylic and sulfonic acids, among other acids tested were saccharin, uric and cyanuric acids.[2] Of these the last two gave compounds which melted above 280° or not at all.

Barbituric acid and its derivatives, in which the acidic hydrogens are capable of replacement by sodium, offered a good chance to see if the reagent could find application here. Especially of interest was the possibility of directly substituting an organic radical in the place of the imide hydrogens, the success of which has, to our knowledge, been recorded in only one instance. Fabre[3] showed that veronal (5,5-diethylbarbituric acid) condenses with two molecules of xanthydrol in the presence of acetic acid to form an insoluble 1,3-disubstituted veronal. We have now succeeded in effecting a similar condensation with *p*-nitrobenzyl chloride in the presence of sodium carbonate (or equivalent base). Acids of the veronal type (both imide hydrogens present) readily give compounds containing one or two nitrobenzyl groups. These are easily soluble in alkali if only one imide hydrogen is replaced or insoluble when both hydrogens are substituted by nitrobenzyl groups.

The compounds formed may be represented by the following probable structural formulas: (A) for the mono-substituted derivative, and (B)


(A)


(B)

for the di-substituted derivative (R = alkyl).

Procedure

The procedure is essentially as described in the previous papers. With compounds suspected of having 2 replaceable hydrogens, *i. e.*, those of the veronal type, about 0.5 g. (approx. 1 equivalent) is taken. To this, in a small round-bottomed flask, is added about 0.25 g. of sodium carbonate and 5 cc. of water. The mixture is warmed to dissolve the acid compound and 0.85 g. of *p*-nitrobenzyl chloride, or equivalent amount of bromide (hereafter designated as reagent), and 10 cc. of alcohol are added. These proportions also hold for compounds of the type where only one methylene hydrogen and one N-hydrogen are still replaceable, and are the proportions generally used for

---

[1] Reid; Lyman and Reid; Lyons and Reid, THIS JOURNAL, 39, 124, 701, 1727 (1917).

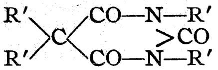
[2] Lyons and Reid, *ibid.*, 39, 1749 (1917).

[3] Fabre, *J. pharm. chim.*, 26, 241 (1922).

totally unknown substances. However, if the compound is suspected of having only 1 replaceable hydrogen the amounts of carbonate and reagent taken are only half of that given above and when there are 3 replaceable hydrogens the amounts of carbonate and reagent are increased by one-half. The mixture thus obtained is refluxed for about an hour. If the p-nitrobenzyl derivative precipitates during the course of the reaction, it is filtered hot on a Büchner funnel. If no precipitate forms, a small sample is cooled. If it still does not precipitate, hot water is added until a cloudiness persists. Cooling then usually gives the desired substance slightly contaminated with some unreacted reagent. The precipitate is washed with water, and more carefully with alcohol and ether and recrystallized as described below.

The various crops of crystals are designated as 1st 1st, 1st 2nd and 2nd 1st, meaning first crystallization first crop and first crystallization second crop, etc. The 2nds were in most instances discarded since high purity rather than quantitative yield was desired. All melting points recorded are uncorrected.

***p*-Nitrobenzyl** Derivatives of Barbituric Acid.—There are four replaceable hydrogens in barbituric acid, making it possible, at least theoretically, to prepare derivatives containing 1, 2, 3 or 4 nitrobenzyl groups. Using 4 equivalents of reagent to one of the acid gave a yellow substance which had no melting point; it charred and burned up. The substance is insoluble in alcohol and ether but is somewhat soluble in chloroform. It is also insoluble in alkali. It probably contains 4 p-nitrobenzyl groups and may be represented by the following structural formula



R' = (—$CH_2C_6H_4NO_2$)

Using less than 4 equivalents of reagent, a mixture of substances was obtained. Besides an insoluble substance having no melting point, a substance soluble in alkali which melted at about 265° was obtained from the mother liquor.

1,3,5,5-Tetra-*p*-nitrobenzylbarbituric Acid.—0.82 g. of barbituric acid dihydrate (1 equivalent) was dissolved in 5 cc. of water containing 0.8 g. of sodium hydroxide (does not dissolve in sodium carbonate solution unless large volume is used). To this were added 10 cc. of alcohol and 3.4 g. (4 equivalents) of reagent. The mixture was refluxed for one hour. It was cooled and the insoluble lemon yellow precipitate was filtered, washed with water, alcohol and ether. The weight was 2 g. It charred when heated. From the mother liquor, on concentration, only some reagent was obtained.

Below are given in tabular form all data relating to the preparation of the p-nitrobenzyl derivatives of barbituric acid and 15 of its alkyl derivatives, and the analyses of several such compounds.

TABLE Ia

EXPERIMENTAL DATA

	"Barbituric acid"	Acid taken, g.	Reagent (R), g.	Na_2CO_3, g.	1st 1st, g.	Final m. p., °C.
1	"Barbituric"	0.82	3.4	0.8	2.0	...
2	"Barbituric"	.92	1.7	.53	0.5	264
3	"Veronal"	.92	1.7	.53	2.0	192
4	"Veronal"	.92	0.86	.27	0.6"	192[a]
5	"Ipral"	.49	0.86	.27	0.8	160
6	"Dial"	1.04	1.71	.53	2.0	190[b]
7	"Neonal"	0.53	0.86	.27	0.7	146
8	"Amytal"	1.1	1.7	.53	.6	138
9	"Butalone"	0.56	0.86	.27	.8	169

TABLE Ia (*Concluded*)

	"Barbituric acid"	Acid taken, g.	Reagent (R), g.	Na_2CO_3, g.	1st 1st, g.	Final m. p., °C.
10	"Luminal"	.58	.86	.27	.6	182
11	5-Ethyl-5-n-amyl-	.55	.86	.27	.7	131
12	1-Methyl-5-hexyl-	.47	.68	.2	.2	139
13	5-Isopropyl-	.56	1.7	.53	.35	187
14	5-n-Butyl-	.3	0.83	.27	.5	180[c]
15	5-Ethyl-1,3-diphenyl-	1.5	1.06	.2	1.0	218
16	N-Methyl-"Veronal"	1.0	0.86	.27	1.5	104
17	N-Ethyl-"Veronal"	1.06	.86	.27	1.5	69[d]
18	N-Phenyl-"Veronal"	0.65	.43	.14	0.5	133

[a] 0.3 g., 148°C. Obtained from the mother liquor, after filtering off the di-(R') derivative, by adding hydrochloric acid and concentrating.

[b] Distinguished from the di-(R') derivative of veronal by its being acted upon by bromine in chloroform.

[c] Use of 3 equivalents of R gave an identical compound.

[d] Reaction mixture crystallized with difficulty.

TABLE Ib

EXPERIMENTAL DATA

	Crystallized from	Resultant product, R′ = *p*-nitrobenzyl: Formula	Resultant product, R′ = *p*-nitrobenzyl: Name, -Barbituric acid
1	...	$C_4O_3N_2R'_4$	1,3,5,5-Tetra-(R′)-
2	H_2O	$C_4H_{4-x}O_3N_2R'_x$	......
3	$CHCl_3$-C_2H_5OH[a]	$C_8H_{10}O_3N_2R'_2$	1,3-Di-(R′)-5,5-diethyl-
4	H_2O	$C_8H_{11}O_3N_2R'$	1-(R′)-5,5-diethyl-
5	$CHCl_3$-C_2H_5OH[a]	$C_9H_{12}O_3N_2R'_2$	1,3-Di-(R′)-5-ethyl-5-*iso*propyl-
6	$CHCl_3$-C_2H_5OH[a]	$C_{10}H_{11}O_3N_2R'_2$	1,3-Di-(R′)-5,5-diallyl-
7	$CHCl_3$-C_2H_5OH[a]	$C_{10}H_{10}O_3N_2R'_2$	1,3-Di-(R′)-5-ethyl-5-butyl-
8	$CHCl_3$-C_2H_5OH[a]	$C_{11}H_{16}O_3N_2R'_2$	1,3-Di-(R′)-5-*iso*-amyl-5-ethyl-
9	$CHCl_3$-C_2H_5OH[a]	$C_{12}H_{10}O_3N_2R'_2$	1,3-Di-(R′)-5-ethyl-5-phenyl-
10	$CHCl_3$-C_2H_5OH[a]	$C_{11}H_{14}O_3N_2R'_2$	1,3-Di-(R′)-5-ethyl-5-butyl-
11	$CHCl_3$-C_2H_5OH[a]	$C_{11}H_{16}O_3N_2R'_2$	1,3-Di-(R′)-5-ethyl-5-*n*-amyl-
12	$CHCl_3$-C_2H_5OH[a]	$C_{11}H_{16}O_3N_2R'_2$	3,5-Di-(R′)-1-methyl-5-hexyl-
13	$CHCl_3$-C_2H_5OH[a]	$C_7H_7O_3N_2R'_3$	1,3,5-Tri-(R′)-5-*iso*propyl-
14	$CHCl_3$-C_2H_5OH[a]	$C_8H_9O_3N_2R'_3$	1,3,5-Tri-(R′)-5-*n*-butyl-
15	$CHCl_3$-C_2H_5OH[a]	$C_{18}H_{15}O_3N_2R'$	5-(R′)-5-ethyl-1,3-diphenyl-
16	C_2H_5OH	$C_9H_{13}O_3N_2R'$	1-(R′)-3-methyl-5,5-diethyl-
17	C_2H_5OH	$C_{10}H_{15}O_3N_2R'$	1-(R′)-3,5,5-triethyl-
18	C_2H_5OH	$C_{14}H_{15}O_3N_2R'$	1-(R′)-3-phenyl-5,5-diethyl-

[a] Dissolved in chloroform and precipitated by the addition of alcohol.

Analyses of several derivatives were performed by Mr. Edward G. Jones, using the Forster modification of the Kjeldahl method.

Anal. 1,3-Di-*p*-nitrobenzyl-5,5-diethylbarbituric acid. Subs., 0.2302, 0.2455: 20.66, 21.52 cc. of 0.1 N acid. Calcd. for $C_{22}H_{22}O_7N_4$: N, 12.34. Pound: N, 12.20, 12.27.

Anal. 1-*p*-Nitrobenzyl-3-phenyl-5,5-diethylbarbituric acid. Subs., 0.2120: 16.02 cc. of 0.1 N acid. Calcd. for $C_{21}H_{21}O_5N_3$: N, 10.63. Found: N, 10.56.

Anal. 3,5-Di-*p*-nitrobenzyl-1-methyl-5-hexylbarbituric acid. Subs., 0.1618: 13.10 cc. of 0.1 N acid. Calcd. for $C_{25}H_{28}O_7N_4$: N, 11.30. Found: N, 11.39.

Summary

p-Nitrobenzyl chloride is a useful reagent for the identification of alkyl barbituric acids. It reacts with these acids, in the presence of sodium carbonate, to form crystalline substitution products with definite melting points. It reacts not only with the imide hydrogens but also with the methylene hydrogens to give completely substituted derivatives.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF CORNELL COLLEGE AND THE UNIVERSITY OF IOWA]

FACTORS INVOLVED IN THE PREPARATION OF MERCURY DI-ISOBUTYL BY THE REACTION OF FRANKLAND AND DUPPA

BY HARRY F. LEWIS AND EUNICE CHAMBERLIN

RECEIVED SEPTEMBER 11, 1928 PUBLISHED JANUARY 8, 1929

In connection with an investigation involving the preparation of the sodium alkyls, it became necessary to make a large quantity of mercury di-isobutyl.[1] The mercury dialkyls have been known since the time of Frankland and Duppa,[2] who prepared mercury dimethyl and mercury diethyl by the action of dilute sodium amalgam on the alkyl iodide in the presence of ethyl acetate. The preparation of mercury di-isobutyl by this reaction has been studied in some detail and the results are given in this paper.

Other dialkyls prepared by the same reaction include the di-*iso*butyl,[3] the di-octyl,[4] the di-*n*-butyl,[5] and the dipropyl and di-isopropyl derivatives.[6] More recently, Marvel and Gould[7] have prepared the methyl, ethyl, n-propyl, isopropyl and n-butyl mercury di-alkyls through the use of the Grignard reagent with the mercuric halide, and Marvel and Calvery[8] the di-*sec.*-butyl, di-*sec.*-octyl, di-*tert.*-butyl and di-*tert.*-amyl derivatives.

Discussion of Experimental Work

In developing the best conditions for the preparation of mercury di-isobutyl by the Frankland and Duppa reaction, a number of variables

---

[1] It is needless to add that mercury di-isobutyl is extremely poisonous. The compound is volatile and ill effects are not noticed at the time. Symptoms of poisoning include severe headaches, disorder of the digestive tract and a sensitivity both toward the odor and taste of the compound in the atmosphere of the laboratory. Continued exposure to the action of the mercury alkyls may result in a degeneration of the central nervous system and brain.

[2] Frankland and Duppa, J. Chem. *Soc.*, 16, 415 (1863); Ann., 130, 104 (1864).

[3] Cahours, Compt. rend., 76, 133 (1873).

[4] Eichler, *Ber.*, 12, 1880 (1879).

[5] Tiffeneau, *Bull. soc. pharmacol.*, 28, 65 (1921).

[6] Goret, *ibid.*, 29, 197 (1922).

[7] Marvel and Gould, THIS JOURNAL, 44, 153 (1922).

[8] Marvel and Calvery, *ibid.*, 45, 820 (1923).

were studied. These include the influence of time of reaction and temperature, relative concentrations of alkyl halide, amalgam and ethyl acetate, the replacement of iodide by bromide and of ethyl acetate by other esters and other compounds containing the carbonyl group.

Standard Procedure

The standard procedure developed as best for the preparation of mercury di-isobutyl is as follows.

A 2-liter round-bottomed flask is set up in an ice-bath and equipped with a 150-cc. dropping funnel, thermometer, reflux condenser and mechanical stirrer. The non-condensable gases are passed through cold concentrated sulfuric acid and then through a spiral condenser at –10°. In the flask are placed 0.294 mole (31 cc.) of isobutyl iodide and 0.147 mole (14.3 cc.) of ethyl acetate. When the mixture cools to the temperature of the ice-bath, a 0.25% sodium amalgam made by adding 0.591 mole (13.6 g.) of sodium to 27.2 moles (5440 g. or 400 cc.) of mercury is run in at such a rate that the temperature of the mixture does not go above 15°. The amalgam in the dropping funnel is protected from moisture in the air by means of a calcium chloride tube.

When the amalgam is added (this takes about forty-five minutes), the flask is disconnected, a layer of ether added and the excess sodium in the amalgam destroyed by the addition of water. The layers are separated in a thick-walled separatory funnel, the ether layer is dried with calcium chloride and fractionally distilled. Mercury di-isobutyl is collected between 202 and 206°.

Variables

Time.—The desired reaction appears to proceed rapidly and is complete as soon as the last of the amalgam has been added. Under the standard conditions a yield of 56.5% of mercury di-isobutyl is obtained. Refluxing the mixture until the total reaction time is two hours does not increase this yield.

Temperature.—Low temperatures favor the formation of the mercury di-isobutyl to a slight extent. With temperatures between 0–5° the yield is 56.5%, between 15–20°, 49% and at the reflux temperature (75–85°) it falls off to 45%.

Molecular Ratio of Reagents

Sodium.—A variation in quantity of sodium, the other factors being kept constant, is permissible to a certain degree. In the standard procedure, two moles of sodium to one of isobutyl iodide are used. Doubling the quantity of sodium to increase the ratio to 4:1 brings the yield down from 56.5 to 50.7%. When the ratio is decreased from 2:1 to 1.1:1, the yield is 48.7%. This is about the lowest ratio to give good results and indicates that a molar concentration of 1:1 moles of sodium may be used when the concentration of the amalgam is approximately 0.14% by weight.

Molar Ratio of Mercury.—Considerable decrease in yield is noted when the volume of mercury is doubled while the weight of sodium is constant. When 800 cc. of mercury is amalgamated with the standard amount of sodium, the weight concentration of the amalgam becomes 0.125%; this amalgam gives but 38.3% of mercury di-isobutyl.

Nature and Amount of Catalyst.—A half mole of ethyl acetate referred to the iodide (ratio 1:2) gives the optimum yield of 56.5%. A molar ratio of 1:1 gives but 48.7%; on the other hand, a ratio of 1:10 (cf. Tiffeneau, ref. 5) forms but small quantities of the desired product.

In the absence of ethyl acetate, mercury di-*iso*butyl is not formed.

A 1:1 ratio of ethyl butyrate with isobutyl iodide gives a 45% yield, while the i:2 ratio forms but 20.4%.

Catalysts Other than Esters.—Other substances containing the tarbonyl radical may be used as catalysts in place of the esters. Such substances include aldehydes, ketones and anhydrides.

Acetone.—A 1:1 molar ratio of acetone to *iso*butyl iodide gives a 50% yield of mercury di-isobutyl, while a 1:2 ratio forms 42.7%.

Isovaleraldehyde.—*Iso*valeraldehyde will also act as a catalyst in the production of the desired compound but the formation of condensation products interferes with the separation of the mercury di-isobutyl.

Stnaller amounts of mercury di-isobutyl result when the ester is replaced by acetic anhydride.

It would thus appear that the carbonyl radical plays an important part in the formation of mercury di-isobutyl from the action of sodium amalgam on isobutyl iodide. This enlarges the statement found in the literature to the effect that "the reaction takes place only in the presence of an ester like methyl or ethyl acetate."[9]

The function of the carbonyl compound is uncertain. In many cases it is apparently used in the reaction and may not be entirely recovered.

Use of **Isobutyl** Bromide.—When the iodide is replaced by the bromide and the reaction carried out as usual, either for forty-five minutes or for a much longer period, only traces of mercury di-*iso*butyl are obtained; the bromide in these cases may be recovered unchanged.

It makes very little difference whether the amalgam is added to the mixture of catalyst and iodide or whether the reverse procedure is used. The yield is the same in either case. The standard procedure is preferred since it is easier to stir the mixture when it is added in this order.

In the original method as proposed by Prankland and Duppa, the reagents were all shaken together in a separatory funnel. This is difficult to accomplish when large quantities of amalgam are used. It is also hard to control experimental conditions and so the yields are found to vary.

The principal by-product in the reaction is di-isobutyl formed as the result of the Wurtz reaction. There is no evidence of the formation of isobutane and very little for the presence of isobutene among the reaction

---

[9] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog *Co.*, Inc., New York, p. 26–27.

products. A purple color in the sulfuric acid wash bottle suggests that the iodide is being carried over.

Conclusions

1. A convenient method has been described for preparing mercury di-isobutyl by the method of Frankland and Duppa. Yields of 50–55% may be obtained.
2. Other esters may be used in place of ethyl acetate. The discovery has been made that carbonyl compounds other than esters can be used as catalysts in the reaction.
3. The principal by-product is di-isobutyl formed by the Wurtz reaction between sodium and isobutyl iodide.
4. Bromide may not replace iodide under the experimental conditions described.
5. Optimum yields are obtained when the following molar concentrations are used: one mole of isobutyl iodide, two moles of sodium, one half mole of ethyl acetate or one mole of acetone and forty six moles of mercury.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 591]

THE DISRUPTION OF THE CORN STARCH GRANULE AND ITS RELATION TO THE CONSTITUENT AMYLOSES[1]

BY T. C. TAYLOR AND C. O. BECKMANN

RECEIVED SEPTEMBER 11, 1928 PUBLISHED JANUARY 8, 1929

In some earlier work in this Laboratory, a method for separating the amyloses in corn starch was devised[1a] and the amount of the insoluble or α-amylose and the soluble or β-amylose determined for corn and other starches. This separation, like all other separations, has as its first step the disruption of the granule in water in order to make available the constituent amyloses in the resulting paste. The completeness of the disruption in this case was gaged by the absence of the characteristic granules under the microscope. To obtain the proper type of paste it was necessary to pre-treat the starch with alcoholic hydrogen chloride and then use an effective swelling agent like ammonium thiocyanate to break open the granules when water was added subsequently.

The primary purpose of this paper is to show that the amount of the amyloses in a given starch, such as that of corn, is not dependent on any specific chemical action of the above reagents but only on their effective-

The work covered in this paper is taken from a part of a dissertation presented by C. O. Beckmann to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[1a] Taylor and Iddles, *Ind. Eng.* Chem., 18,713 (1926).

ness in causing complete rupture of the granule. Other swelling agents or mechanical abrasion give starch pastes from which the amyloses may be separated in the same proportion as found previously, whenever such pastes contain no unbroken granules. It is taken for granted that in all methods hydrolytic decomposition or dextrinization must be avoided.

Proof of correctness of this point of view comes from a detailed study of the constitution of a starch paste as a function of swollen granules and of constituent amyloses after their liberation through rupture of these granules. Discrepancies in the literature with regard to the amount of amyloses can be accounted for and avoidance of these difficulties made possible, it is felt, by the results of the investigation. As will be seen, a combination of microscopic examination, viscosity and amylose determination is used to **fix** the properties of the paste and give the picture we have drawn.

Before proceeding it might be well to set down briefly for purposes of reference two current interpretations of the mechanism of paste formation. It is believed by many[2] that the mechanism of paste formation consists of the imbibing of water by the granule, usually by heating, the swelling of the granule, its bursting, the leaching out of the inner substance and, upon cooling, the setting of this material to a viscous gel.

This gel is generally supposed to consist of two parts, separable because of their different solubility in water, but here is where the difficulty begins, for even with the same starch, for example, potato, the amount of insoluble material is reported as varying from 80% down to 2% (the soluble material by difference).[1a,3]

On the other hand, there are those[4] who apparently regard starch as a single chemical individual which in water becomes soluble to a greater or less extent due to hydration. According to this view a starch paste would consist of an equilibrium mixture of more or less hydrated forms of the one substance. The discrepancies in the ratio of insoluble to soluble portions can be explained as a shifting of the equilibrium point due to the imposed conditions.

That there are at least two fairly well defined constituents of the starch granule has been repeatedly demonstrated and is now generally accepted by most investigators[6] While these amyloses probably do hydrate to a

---

[2] See Haas and Hill, "An Introduction to the Chemistry of Plant Products," Longmans, Green and Co., London, 1921, Vol. I, pp. 112–118.

[3] (a) Maquenne and Roux, *Compt. rend.*, 140, 1303 (1905); (b) Gatin-Gruzowska, *ibid.*, 146, 540 (1908); (c) Tanret, Bull. *soc. chim.*, *[4]17*, 83 (1915); (d) Sherman and Baker, THIS JOURNAL, 38, 1885 (1916); (e) Ling and Nangi, J. *Chem. Soc.*, 124, 2666 (1923).

[4] (a) Fouard, *Bull. soc. chim.*, 3, 1170 (1908); (b) Harrison, J. *Soc. Dyers Colourists*, 32, 40 (1916).

[5] See R. P. Walton, "A Comprehensive Survey of Starch Chemistry," Chemical Catalog Co., New York, 1928.

different degree, the following observations indicate that the explanations for the discrepancies in the ratio of the amyloses, at least in corn starch, come from a consideration of the physical condition of the paste from which they are separated rather than from differences in degree of hydration or the presence of a large number of amyloses mutually transferable one into the other. In this respect our results bear out quantitatively the observations and conclusions of Alsberg on the properties of a starch paste.[6]

In this Laboratory it has always been noticed that when amyloses were separated from a paste of high viscosity the amount of insoluble material (classed as a-amylose) was high and whenever pastes of the same concentration were made that were limpid (low viscosity) the insoluble portion was low. Since under the microscope the highly viscous pastes as well as the separated, insoluble material from them showed large quantities of unbroken granules, it was concluded that the amount of so-called α-amylose so determined was fictitious. Contrariwise, in the limpid pastes as used by Taylor and Iddles,[1a] no characteristic granules can be observed under the microscope and the amount of insoluble material is relatively low (amount of soluble or β-amylose is correspondingly high).

Apparently, high paste viscosity, non-availability of the soluble amylose and swollen granules are definitely interrelated. That this is so is borne out by some quantitative measurements given later. It will be shown that the viscosity of pastes made from separated amyloses in a given concentration is only slightly greater than that of water, while that of pastes of the same concentration made by gelatinization[7] is relatively high.

These observations lead logically to another picture[6] of a starch paste, namely, that in the gelatinization of whole starch by hot water some granules only swell while others rupture. The number swelling and the number rupturing depend on the previous treatment given the raw starch or on treatment of the paste. On this basis the viscosity would be due almost entirely to whole but swollen granules[S] which still contain their quota of constituent amyloses. As will be seen, complete rupturing or even partially complete rupturing of the granules is not easily accomplished."

---

[6] Alsberg, *Ind. Eng. Chem.*, *18,* 190 (1926).

[7] The term "gelatinization" should not be confused with disruption of the starch granule. Frequently the terms are used interchangeably. In the course of this research it was found that, although related, they are by no means the same thing. To differentiate between them, therefore, gelatinization will be defined simply as the swelling of the granules, while disruption will mean the actual breaking up of the granule.

[8] Harrison, *J. Soc. Dyers Colourists*, *27,* 84 (1911).

[9] Pastes made in the usual way by boiling the starch with water either at atmospheric pressure or in an autoclave at 15 pounds above atmospheric (to get the corresponding increased temperature) contain swollen granule.; in large quantities. Long treatment under these conditions causes the granules to swell to such an extent that their index of refraction becomes almost that of water and they can be observed only after staining with iodine or gentian violet.

Experimental Part

Effect of Swelling Agents.—Repetition of the work of Taylor and Iddles[1a] on corn starch but omitting the pre-treatment with alcoholic hydrogen chloride gave a stiff paste, instead of the limpid one they describe, on the addition of ammonium thiocyanate. The acid apparently contributes to the process of rupturing also. Substitution of potassium iodide[10] for the ammonium thiocyanate in the Taylor-Iddles''' method gave the same amount of the amyloses as found by them.

A good grade of alkali-washed corn starch was treated with an alcoholic-hydrochloric acid solution according to the method.''' Sixty grams of this sample was treated with a solution of 46 g. of potassium iodide, 46 g. of water and 37 cc. of 95% alcohol. The starch was added to this solution in small portions with constant stirring and rubbing until a homogeneous suspension was formed. Alcohol was added to precipitate the starch after microscopic observation showed that no more whole granules existed. The precipitated, gelatinous mass was ground in a mortar with portions of alcohol until it became granular. It was then washed repeatedly with hot alcohol to remove the potassium iodide, which gave the starch a slight yellow color. It was found impossible to remove the potassium iodide completely. Refluxing the sample in a Soxhlet extractor with alcohol for seventy-two hours failed to remove it. About 10–14% of potassium iodide was absorbed by the starch. The determinations of p-amylose by ultrafiltration made on these samples were corrected, therefore, for absorbed salt: β-amylose found, 85%.

Other swelling agents such as ammonium nitrate or zinc chloride, although effective, were disregarded either because they could not be removed or corrected for subsequently or else because they had a tendency toward the promotion of amylose hydrolysis. The latter reaction is the one that must be avoided. Even the pre-treatment with alcoholic hydrogen chloride gives some substances that reduce Fehling's solution[8] and causes the liberation of some of the associated fatty acids.[11] The amount of the starch so affected is very small and in the light of the subsequent work may generally be neglected.

Mechanical Rupture of Granules in Paste.—If the viscous paste made by heating 5 g. of dry, untreated corn starch with water in the usual way is shaken[4b] or ground in a pebble mill,[12] it becomes more limpid. This may be interpreted as a breaking of some of the swollen granules. Other and perhaps more strenuous methods ought to bring about rupture of all the granules. Accordingly, a similar paste was passed six times through an homogenizer[13] where at a pressure of 4000 lb. per square inch it was discharged through a small outlet orifice.

---

[10] Reychler, Bull. *soc. chim. Belg.*, **29**, 118 (1920).

[11] Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); Taylor and Lehrman, *ibid.*, **48**, 1739 (1926).

[12] Alsberg and Perry, *Proc. Soc. Exptl. Biol. Med.*, **22**, 60 (1924).

[13] A Colony homogenizer used for making emulsions was employed. The authors wish to thank Pease Laboratories, Inc., New York City, for the use of this machine and also Messrs. Knoll and Stone for their assistance.

Under the microscope even on stained samples no characteristic granules could be seen in this paste, but the striations so characteristic of the whole granule were very much in evidence. The insoluble or α-amylose as determined by the electrophoretic method of Taylor and Iddles[1a] was 62.5%, while they report 15%. A comparison of the viscosities of this paste with that of raw starch and of the two amyloses under identical conditions and at the same concentrations (see Table I) shows the homogenized paste to be nearer that of raw starch. Apparently this treatment distorts but does not rupture a large number of the already swollen granules, hence the striations, high viscosity and large amount of insoluble "α-amylose." Of course some of the swollen granules are broken and whatever soluble material (β-amylose) is in solution would come, according to our point of view, from these disintegrated starch particles. Further work corroborates this hypothesis.

Disintegration of Dry Granules by Grinding.—It was evident from the results of the previous attempts that breaking swollen starch granules in a paste is not so easily accomplished. Grinding dry starch with sand and subsequently leaching out the soluble material (β-amylose) has been practiced.[14] Alsberg and Perry[15] report that pastes made from dry wheat starch ground in a pebble mill are less viscous than those from unground starch. Prom these ground samples, moreover, much more soluble material was obtained than from the unground by extraction with water at room temperature. They note also that after grinding in a pebble mill for a certain period there are still grains which like the whole starch are birefringent and show the characteristic black cross under the polarizing microscope.[16]

This method of pre-treatment of corn starch seemed to offer great promise in the present problem for it would eliminate completely the necessity for using chemical swelling agents in making the pastes. Suspicion of possible chemical changes in the amyloses would then be removed and the significance of viscosity measurements made more sure. Therefore a series of experiments was made substituting grinding in a ball mill for the use of swelling or gelatinizing agents in the Taylor-Iddles[1a] method. Comparisons were made of the viscosities of pastes from whole starch, with those from samples after various periods of grinding. These results were correlated with the microscopic appearance and with the amount of β-amylose which could be extracted with cold water from the sample or separated from it by electrophoresis. Later the viscosity of the amyloses themselves which had been separated by the electrophoretic method of Taylor and Iddles[1a] from a paste made from a completely ground sample was determined.[17]

---

[14] Delffs, *Pogg. Ann.*, *109*, 648 (1860).

[15] Alsberg and Perry, *Proc. Soc. Exptl. Biol. Med.*, **22**, 60 (1924).

[16] Reichert, Carnegie Publication No. 173, pt. 1.

[17] In a strict sense it is incorrect to speak of the viscosity of a starch paste because

The ground samples were prepared finally as follows. Three hundred g. of dry corn starch was put in a four-gallon ball mill with about the same volume of quartz balls averaging about $^3/_4$ inch in diameter. The mill was rotated at 45–55 r.p.m. for the periods of time indicated. Twelve-hundred-g. starch loads were used at first but the load was reduced to 300 g. and the grinding continued. If 300 g. is the initial load birefringence disappears and the value for β-amylose reaches 85% after about 172 hours of grinding.

Soluble β-amylose was determined as follows: 2–3 g. of dry starch is shaken with water in a graduated flask and the volume made up to 500 cc. A small amount of toluene is added to prevent the growth of molds. The insoluble part settles out. When a clear supernatant liquid is obtained, an aliquot portion is removed with a pipet to a weighed evaporating dish almost filled with dry sand. This is put into an oven at 105° and evaporated to constant weight, which usually takes three hours.

After grinding the 1200 g. of starch for 130 hours, microscopic examination showed whole granules in large quantities and extraction gave 51.3% β-amylose. After 225 hours' total grinding, no characteristically shaped granules were apparent but birefringence, as evidenced by black crosses in the polarizing microscope, were still plainly visible. The β-amylose (soluble material by extraction) had risen to 63.1%. To cut down the time of treatment, 300 g. of this starch and the same ball load were ground an additional 325 hours, making the total period of 600 hours. In this sample there were no birefringent granules noticeable and the soluble β-amylose (fatty acid free) was 84.1%.

It is interesting to note that when birefringence disappears the amount of soluble or β-amylose is the same as that found by Taylor and Iddles.[1a] Before that point the granules, although no longer characteristically shaped (due no doubt to the effects of the beating in the mill), still hold in a coherent form from their quota of amyloses.[4b] By an electrophoretic separation about 11% of the a-amylose was found in the paste of the 600 hour sample by Taylor-Iddles.[1a] Continued grinding led to the formation of highly opalescent solutions which contained nearly 2% of silica from abrasion of the balls. While not significant in this connection the effect of long grinding on the insoluble a-amylose is being studied.

TABLE I

RELATION BETWEEN PRE-TREATMENT, AVAILABLE β-AMYLOSE AND VISCOSITY

Pre-treatment of corn starch	β-Amylose, %	Relative viscosity at 35°; 1% paste
(a) None	...	2.09
(b) Alc.-HCl and NH_4CNS according to ref. 1a	85.0	1.05
(c) Orig. ground 130 hours	51.3	1.39
(d) Orig. ground 225 hrs.	63.1	1.32
(e) Orig. ground 600 hrs.	84.1	1.09
(f) β-Amylose from (b) by electrophoresis	100.0	1.07
(g) β-Amylose from (e) by electrophoresis	100.0	1.08

---

of its heterogeneity, but it will be shown that settling has no appreciable effect on the values of viscosity relative to water in the concentration used.

Passing to a study of the viscosities of these pastes the results shown in Table I were obtained.

One-tenth of a gram (for a 1% paste or solution) of dry powdered sample was put into an ordinary test-tube and 10 cc. of distilled water added. The tube was then immersed in a beaker of boiling water. After one and one-half minutes the tubes were removed, shaken for ten seconds and re-immersed. After three minutes this was repeated and at the end of five minutes the tube was removed to a thermostat and allowed to come to temperature at 35°. After having attained the temperature of the thermostat, 5 cc. of the paste was removed to an Ostwald viscometer (of the ordinary type with a capillary 10 cm. long and a time value for water at 35° of about sixty seconds). Five to seven readings were taken on each sample. The time for a complete determination is from twenty to thirty minutes from the time of heating. Settling, which would obviously change the time of flow through the capillary, is negligible, since it can be noticed only after fifteen to twenty hours of standing. Moreover, deviations in a set of readings seem to be entirely independent of time.

Precision of Viscosity Measurements

Each value for relative viscosity is the average of those obtained on at least two samples. Each sample was run through the Ostwald viscometer 5 to 6 times. The average deviation for these 5 to 6 runs was 1–2%. The average deviation between two samples prepared (for viscosity measurements) independently was 3–4%.

This accuracy was not obtainable for relative viscosities above 7 or 8. The average deviation in these cases was about 6–7%.

The temperature at which the viscosities were run was 35 ± 0.05°. The change of viscosity due to temperature over this small range was found to be negligible.

In every case the a-amylose which carried the associated fatty acids is equal to (100 − β). When extraction is used the β- is determined directly but in (b) and (d) it was easier to determine the *a*- directly. In (e) a direct current potential of 1200 volts was used to hasten the migration. This gave a clear, supernatant liquid which contained all of the β-amylose **(g).** A layer of toluene on the surface of the liquid prevented mold formation. Incidentally, a similar sample in water under toluene showed no signs of settling after standing for three months. This illustrates how the application of the direct current potential facilitates separation.

Dry samples of β-amylose were obtained by precipitation, on the addition of alcohol to the clear water solutions. The α-amylose was removed from the bottom of the electrophoretic cell[1a] and partially dehydrated by the addition of alcohol. In both cases, to remove the remains of water and obtain a granular mass, a mixture of benzene and alcohol was added in successive portions with mechanical stirring after each portion, forming the ternary mixture (water–benzene–alcohol), boiled off at 60°. The final treatment leaves the white, amorphous material behind in absolute alcohol, from which it is recovered by filtration and evaporation of the adhering alcohol at room temperature.

It should be noted that only when the viscosity has dropped to almost that of the amyloses themselves does the total β-amylose become available for separation from the paste. Of course the rather slimy, insoluble α-amylose contributes something to the viscosity of more concentrated pastes, but it is present in corn starch only to the amount of 15%. In mixtures of α- and β-amyloses in the proportion in which it exists in corn starch in pastes containing 1% total solids, the viscosity was practically that of β- alone and did not approach that of a heat-gelatinized whole starch of the same concentration. These results support the contention that the viscosity of an ordinary starch paste is due to the undisintegrated granule. More significant for the present purpose, however, is the fact that a paste made from a completely ground starch when subjected to the Taylor-Iddles[1a] method gives the same ratio of amyloses with the same general properties as that obtained from their ammonium thiocyanate treatment.

In these measurements it must be remembered that corn β-amylose has a solubility of 7 g. per 100 cc. at 25° and 10 g. per 100 cc. at 35°. These solutions are perfectly clear, but above the concentrations at the respective temperatures there is cloudiness and settling. This, of course, makes viscosity determinations of little quantitative use in this range. In the following table there are summarized the results of the observation.

TABLE II

VARIATION OF VISCOSITY WITH CONCENTRATION AT 35°

Concn. %	Raw starch	Ground starch (63.1% sol.)	β-amylose (from ground starch)
0.25	1.14	..	...
0.50	1.35	..	...
1.00	2.09	1.31	1.078
2.00	7.24	1.71	1.182
3.00	38.95	2.43	1.277
4.00	paste	3.39	1.396
5.00	too	4.77	1.512
6.00	stiff	6.41	1.667
7.00	..	..	1.807
8.00	..	..	1.986
9.00	..	..	2.117
10.00	..	..	2.308

From the above table it is evident that it takes about ten times as much β-amylose (in solution) as it does gelatinized raw starch to obtain the same viscosity. Because of the insolubility and rapid settling of the *a*-amylose, there is no way by this method of measurement, to tell how much this substance contributes to the viscosity of a partially ruptured paste (as in third column). For comparison in a qualitative way, however, these results are interesting.

Summary and Conclusions

1. It has been shown that the a- to β-amylose ratio in corn starch as determined previously[1a] is not dependent upon the method of treatment.

2. Complete rupture of the starch granule may be accomplished also by grinding. The product of this method yields amyloses of high purity.

3. Additional proof is brought forward that the viscosity of a starch paste is directly connected with the number of swollen granules (gelatinized) in that paste.

4. The structure of starch pastes has been discussed and it has been shown that its characteristic properties in the case of corn are functions more of the physical nature of the starch granules than of the chemical nature of the amyloses.

5. The results indicate that before a separation of the constituent amyloses in corn starch can be made, all of the granules must be ruptured. This is evidenced by a drop in the viscosity of starch pastes. Any attempts at separation before this point result in fictitiously high results in insoluble material. Although a few granules rupture easily, the great bulk do so only with great difficulty when a paste is made in the ordinary way.

NEW YORK CITY

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XX. PREPARATION, PROPERTIES AND IDENTIFICATION OF GLYCEROL BETA-METHYL ETHER

BY HAROLD HIBBERT, MYRON S. WHELEN[1] AND NEAL M. CARTER[2]

RECEIVED SEPTEMBER 13, 1928 PUBLISHED JANUARY 8, 1929

The important role played by glycerol esters and ethers in animal metabolism, industrial processes and organic research has led various investigators to point out the necessity for a reliable characterization of a series of readily identifiable, simple derivatives of glycerol containing substituents definitely located in the a-, β- and a'-positions.

For reasons defined later in this paper, the glycerol ethers are probably the most suitable for the preparation of such a series. Thus Irvine, Macdonald and Soutar[3] proposed the use of glycerol α,β- and α,α'-dimethyl ethers and a- and 8-monomethyl ethers for the identification of mixed glycerides. Controlled hydrolysis of glycerides followed by methylation and further hydrolysis, with the aid of the above reference types, would serve to identify the configuration of the original glyceride substituents.

---

[1] Holder of Bursary from Canadian National Research Council.

[2] Research Fellow, Department of Industrial and Cellulose Chemistry, McGill University, Montreal.

The authors desire to express their appreciation of the facilities afforded them in carrying out this work, on the one hand to the Canadian National Research Council for the gift of a Bursary (M. S. W.) and on the other to The Forest-Products Laboratory of Canada and the Canadian Pulp and Paper Association for valuable assistance.

[3] Irvine, Macdonald and Soutar, J. Chem. *Soc.*, 107, 342 (1915).

Later, Gilchrist and Purvis[4] attempted to prepare such a series for the identification of the products obtained by the hydrolysis of methylated glycerol glucosides, but were unable to prepare the α,α′-dimethyl and the β-monomethyl ethers. Of the five possible glycerol methyl ethers, the trimethyl,[5] the α,β-dimethyl,[5] a,α′-dimethyl[6] and α-monomethyl[7,8] have been described.

The recent preparation in this Laboratory[9] of the missing member of this series, glycerol β-methyl ether, is thus of considerable interest as it is believed to be the first preparation of a pure @-ether of glycerol. For purposes of ready identification, three crystalline derivatives of this have been prepared, the properties of which are summarized in the following table. The corresponding derivatives of the isomeric a-methyl ether are added for comparison.

Derivative	Of glycerol a-methyl ether, m. p., °C.	Of glycerol @-methylether, m. p., °C.	Crystallizing medium
Di-*p*-nitrobenzoate.	108	155	Ethyl acetate
Di-phenylcarbamatc.	118–119	102	Benzene-ligroin
p-Nitrobenzylidene acetal......	42; 47	106; 139	Methyl alcohol

The di-benzoates appear to be liquids. In the following table a comparison is given of the properties of the glycerol a- and β-methyl ethers.

	Glycerol a-ether	Glycerol @-ether
Boiling point...................	110–111° (13 mm.)	122–123° (13 mm.)
Refractive index$^{17°}_{D}$..............	1.4463	1.4505
Density$^{17°}_{4°}$.....................	1.1197	1.1306

Both ethers are readily soluble in water and most organic solvents The constants of the a-ether are those found by Irvine and co-workers,[8] while those of the β-ether are the results obtained in the preparation of the β-ether by three different processes in this Laboratory.[9,10]

Various *β-esters* of glycerol have been described in the literature,[11] such as the β-nitrate,[12] β-phosphate,[13] β-margarate,[14] β-palmitate,[15] β-benzo-

---

[4] Gilchrist and Purvis, J. *Chem. Soc.,* 127,2738–2739 (1925).

[5] Gilchrist and Purvis, *ibid.,* 127, 2743–2744 (1925).

[6] Zunino, *Atti Accad. Lincei.,* [5]6, II, 348 (1897).

[7] Grün and Bockisch, *Ber.,* 41, 3471 (1908).

[8] Irvine, Macdonald and Soutar, J. *Chem Soc.,* 107, 337 (1915).

[9] Hill, Whelen and Hibbert, THIS JOURNAL, 50,2235 (1928).

[10] (a) Hibbert and Carter, *ibid.,* 50,3120 (1928); *(b)* Hibbert and Carter, *ibid.,* 50, 3376 (1928).

[11] In a previous communication, *ibid.,* 50, 2238 (1928), the statement was made that "glycerol β-methyl ether marks the first definite β-derivative of glycerol to be recorded in the literature." In order to avoid any misunderstanding it should be clearly stated that this remark had reference only to the alkyl ethers of glycerol.

[12] Will, *Ber.,* 41, 1120–1122 (1908).

[13] Tutin and Hahn, J. *Chem. Soc.,* 89,1755 (1906).

[14] Thompson, *Trans. Roy. Soc. Canada,* [iii]20,449 *(1926).*

[15] Grün, *Ber.,* 43, 1288 (1910).

ate[16] and others, and many methods have been advanced for the synthesis of mixed glycerides with substituents in various positions for comparison with natural products.[14,17] Recent papers,[18] however, cast considerable doubt on the validity of any method involving the intermediate use of halohydrins, and particularly the α,α'-dichloro- or dibromohydrin utilized in the preparation of most of the above compounds, since the products obtained proved to be not the β-derivative but the corresponding a-isomer, in other words a "group wandering" had occurred.

Thus the failure of Gilchrist and Purvis[5] to obtain α,α'-dimethyl and β-monomethyl ethers of glycerol by methods analogous to those used in preparing the above glycerides and other representatives of the series of ether was attributed by them[4] to a wandering of the halogen or methyl group. Similar wandering of acyl groups has been reported[17b,19] in the interesting investigation carried out by Grün and co-workers.

All of these facts focus attention upon the importance of using glycerol ***ethers*** as reference compounds for the determination of configuration, since a wandering of an alkyl group has not been observed in this connection. The authors believe that the methods used for the preparation of glycerol 0-methyl ether described in this paper are generally applicable for the detection of all β-glycerol ethers and glucosides.

Experimental Part

Preparation of Di-p-nitrobenzoate of Glycerol or-Methyl Ether.—The glycerol a-methyl ether used in this experiment was prepared by two methods: *(a)* hydrolysis of 1,2-*iso*propylidene glycerol 1'-methyl ether;[8] and (b) interaction of glycerol α-chlorohydrin (Kahlbaum) with a methyl alcoholic solution of sodium methylate. Both preparations yielded an identical di-p-nitrobenzoate.

Seven-tenths of a g. of the pure glycerol a-methyl ether was dissolved in 5 g. of dry pyridine and after first heating slightly to start the reaction, 6.5 g. of p-nitrobenzoyl chloride was added in small portions; finally, the whole was heated until the product liquefied. It was then allowed to stand at room temperature for eighteen hours. The pasty mass was well stirred with 250 cc. of $N/10$ sulfuric acid solution at 30° to remove the excess pyridine, washed with dilute sodium bicarbonate, finally with water and dried at 100°. Crystallization from hot toluene first deposited a very small amount of a brownish, amorphous powder, m. p. 188°.[20]

The main product was a definite crystalline compound which on recrystallization from hot toluene separated as yellow needles of m. p. 108"; yield practically theoretical.

---

[16] Helferich and Sieher, Z. *physiol. Chem.*, 175, 311–315 (1928).

[17] (a) Grün, *Ber.*, 54, 273 (1921); (b) Fischer, Bergmann and Bärwind, *ibid.*, 53, 1605 (1920); (c) Whitby, J. *Chem. Soc.*, 128, 1458 (1926); (d) Helferich and Sieber, *Z. physiol. Chem.*, 170, 31 (1927).

[18] (a) Fischer, *Ber.*, 53,1621 (1920); (b) Fairbourne and Foster, J. *Chem Soc.*, 128, 3148–3149 (1926).

[19] Grün and Limpacher, *Ber.*, 60, 147, 151 (1927).

[20] This product is formed when p-nitrobenzoyl chloride and pyridine alone are heated. See in this connection Stather, *Ber.*, **57B,** 1392–1393 (1924); Hermans, Z. *physik. Chem.*. 113, 337 (1924).

Anal. Subs., 0.1527: CO_2, 0.2971; H_2O, 0.0558. Calcd. for $C_{18}H_{16}O_9N_2$: C, 53.48; H, 3.99. Found: C, 53.08, 53.37; H, 4.09, 4.13.

Preparation of **Di-*p*-nitrobenzoate** of Glycerol **β-Methyl** Ether.—The glycerol ether used was obtained by the hydrolysis of 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ether, m, p. 106°.[10b] Another sample prepared by hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether yielded an identical di-p-nitrobenzoate.

Six-tenths of a gram of the glycerol ether was treated in an exactly similar manner to that above, using 5 g. of dry pyridine and 6 g. of *p*-nitrobenzoyl chloride. Only one product was obtained, which on recrystallization from hot toluene separated as small clusters of orange needles, m. p. 155"; yield almost quantitative.

Anal. Subs., 0.1799: CO_2, 0.3548; H_2O, 0.0661. Subs., 0.2299: N, 13 cc. at 25" and 756 mm Calcd. for $C_{18}H_{16}O_9N_2$: C, 53.48; H, 3.99; N, 6.93. Found: C, 53 71; H, 4.11; N, 6.74.

Preparation of the Di-phenylcarbamate of Glycerol a-Methyl Ether, C_6H_5NHCOO-$CH_2CH(OCONHC_6H_5)CH_2OCH_3$.—One and two-tenths g. of pure glycerol a-methyl ether, b. p. 110–111° (13 mm.), (obtained from the hydrolysis of 1,2-benzylidene glycerol 1'-methyl ether) was mixed with 2 moles of phenyl isocyanate, warmed in a water-bath at 60° for a short time and then allowed to stand for several days at room temperature. The liquid reaction mixture changed to a glassy mass. On further standing white crystals were deposited and the whole mixture became solid. This was dissolved in warm benzene and recrystallized from a mixture of benzene and ligroin, b. p. 80–90" (equal parts), yielding very fine white needles, m. p. 118–119°.

Anal. Subs., 0.1430: CO_2, 0.3279; H_2O, 0.0737. Calcd. for $C_{18}H_{20}O_5N_2$: C, 6283; H, 5.82. Found: C, 62.53; H, 5.76.

Glycerol a-methyl ether obtained by the hydrolysis of 1,2-*iso*propylidene glycerol 1'-methyl ether, as well as by the action of sodium ethylate on a-monochlorohydrin, yielded the same product with phenyl isocyanate.

Di-phenylcarbamate of Glycerol **β-Methyl** Ether, $C_6H_5NHCOOCH_2CH(OCH_3)$-$CH_2OCONHC_6H_5$.—One g. of pure glycerol β-methyl ether, b. p. 123° (13 mm.), (obtained from the hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether) was treated with the equivalent amount of phenyl isocyanate in a similar manner. This yielded fine, white needles from benzene-ligroin solution, m. p. 102°.

Anal. Subs., 0.1340: CO_2, 0.3072; H_2O, 0.0722. Calcd. for $C_{18}H_{20}O_5N_2$: C, 62.83; H, 5.82. Found: C, 62.52; H, 6.02.

A mixed melting point determination made with approximately equal quantities of these two di-phenylcarbamates gave a melting point of 90°, showing the non-identity of these two substances.

Preparation of the ***p*-Nitrobenzylidene Acetals** of Glycerol ***a*- and** &Methyl Ethers.—This condensation is probably more readily and quickly carried out than that of either of the above two types of derivatives. Full details and an explanation of the existence of the two pairs of melting points are found in a previous paper.[10b] **A** brief description of the method employed, sufficing for a ready recognition of the two glycerol monomethyl ethers, is given below..

One g. of the glycerol methyl ether is heated with 1.5 g. of pure *p*-nitrobenzaldehyde (1:1 molecular proportions) and a small drop of 40% sulfuric acid (as catalyst) for fifteen to twenty minutes at 110–120°, the container being meanwhile connected to a water suction pump giving approximately 15 mm. pressure. The resulting product is dissolved at 20° in 3.5 cc. of methyl alcohol and allowed to cool overnight at 0° or lower.

Glycerol a-methyl ether when thus treated yields a pasty mass which redissolves in the methyl alcohol on warming to room temperature, but which may be obtained in crystalline form by filtering the pasty mass from the solvent at a low temperature and recrystallizing. The product is a mixture of the two isomeric 1,2-*p*-nitrobenzylidene glycerol 1'-methyl ethers. The isomer melting at 47° always tends to crystallize out first in characteristic short, yellowish prisms, while the second isomer (m. p. 42') separates as white nodules on further cooling.

From the *β*-methyl ether, on the other hand, the methyl alcohol deposits a mixture of the two markedly crystalline isomeric 1,1'-*p*-nitrobenzylidene glycerol 2-methyl ethers (m. p. 139 and 106°). Recrystallization usually first deposits the higher-melting isomer as gray-white needles but, depending on the amount of solvent used, the lower-melting isomer may simultaneously crystallize as short, white prisms. Although these may be readily separated and identified, the melting point of the mixture (approximately 90°) serves to differentiate the product from that obtained from glycerol *α*-methyl ether.

Summary

1. The properties of and methods for identifying glycerol 0-monomethyl ether are described.

2. The importance of the product as a "type substance" in organic analyses and syntheses is indicated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF PHENYL NAPHTHYL KETONES BY THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE

BY W. E. BACHMANN AND R. V. SHANKLAND[1]

RECEIVED SEPTEMBER 28, 1928 PUBLISHED JANUARY 8, 1929

Aromatic ketones[2] are reduced by magnesium + magnesium iodide to free radicals, ketyls, which associate to pinacolates. Addition of water to the pinacolate gives the pinacol. By this method various classes of ketones have been reduced to pinacols. We have now studied the reaction between the binary system and ketones containing a naphthyl group.

We have found that both phenyl a-naphthyl ketone and phenyl P-naphthyl ketone are reduced to the corresponding ketyl pinacolate systems. During the reduction green and brown colors are engendered in the solution. These colors disappear when the solution is exposed to air and reappear when air is prevented from entering. Water likewise removes the color, with concomitant formation of the pinacol.

The pinacol produced from phenyl a-naphthyl ketone by Mg + MgI_2 is different from the pinacol produced from the same ketone by zinc + acetic acid.[3] However, we found that the latter isomer (I) may be trans-

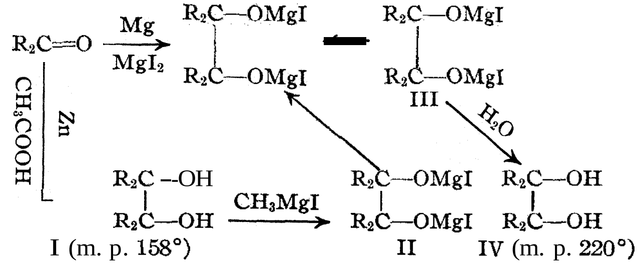
---

Holder of the Prescott Fellowship in Organic Chemistry.

[2] Gomberg and Bachmann, THIS JOURNAL, 49,236 (1927).

[3] Compare the reduction of benzaldehyde which gives rise to mesohydrobenzoin (m. p. 134") and racemic hydrobenzoin (m. p. 119°).

formed into the former (IV) by converting it to its pinacolate (II) by means of a Grignard reagent. Dissociation into radicals takes place[4] and these radicals become identical with those formed by the addition of Mgf to the C=O group of the ketone, and associate to the new pinacolate (III).



Only a single pinacol was produced when phenyl β-naphthyl ketone was reduced by the two different reducing agents.

The pinacols prepared through the agency of the binary system were rearranged to the corresponding pinacolins, and it was found that the naphthyl group wandered in preference to the phenyl group.

Experimental

Reduction of Phenyl α-Naphthyl Ketone

Reduction of the Ketone by Mg + MgI_2.—A colorless mixture of Mg + MgI_2 was prepared from 4.0 g. of magnesium powder and 12 g. of iodine in 75 cc. of anhydrous ether and 75 cc. of dry benzene. To this mixture 10.0 g. of phenyl α-naphthyl ketone was added and the flask was then stoppered and shaken. Almost instantly the solution became olive-green in color and later the color changed to brown. After half an hour the color was a clear green and reduction was considered complete. On exposure to air the green color was quickly destroyed but when the solution was protected from air the green color reappeared. The solution was filtered from the excess of magnesium and was decomposed with ice and ammonium chloride. Experiments in which a rod of magnesium was employed for reduction showed that the magnesium loss was equivalent to 108% of the calculated value, and that the magnesium hydroxide produced on hydrolysis corresponded to 105%. The organic solution was washed with water and dried over sodium sulfate. Evaporation of the solvents at room temperature left an oily residue. The oil was extracted with warm petroleum ether (40–60°) in order to remove unchanged ketone; however, only traces of ketone were found in this extract. During this treatment the oily mass usually solidified. The crude pinacol (9.2 g.) was recrystallized by dissolving it in the minimum amount of hot chloroform, adding twice that volume of hot alcohol and evaporating the solvents until crystallization began. In this way 4.6 g. of pure diphenyl-di-α-naphthyl pinacol was obtained, which represents a yield of 46%. The pinacol crystallizes in glistening prisms, melting at 220° with decomposition.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.32; H, 5.60. Mol. wt., calcd.: 466. Found: 469.

Measurement of the gas evolved when the pinacol was treated with methylmagnesium iodide showed the presence of two hydroxyl groups.

---

[4] Ref. 2, p. 247.

The low yield of pinacol is attributed to difficulty in crystallization. The crude reduction product was shown to be mostly pinacol by rearranging it to the pinacolin. The crude pinacol from 5.0 g. of ketone gave 4.2 g. (87%) of pure pinacolin.

Rearrangement of the Pinacol to the Pinacolin.—The pinacol readily undergoes dehydration when it is warmed with acetic acid containing a small amount of iodine[6] or when it is treated with acetyl chloride. The pinacolin remaining after the solvent had been evaporated was recrystallized from chloroform–alcohol; yield, practically quantitative; m. p. 216–217°. By its reaction with alcoholic potassium hydroxide the pinacolin was proved to be benzoyl-di-a-naphthylphenylmethane $(C_6H_5)(C_{10}H_7)_2CCO(C_6H_5)$.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.94; H, 5.25. Mol. wt., calcd.: 448. Found: 441.

One gram of the pure pinacolin, heated with alcoholic potassium hydroxide for eight hours, gave 0.260 g. (96%) of benzoic acid.

Reduction of the Ketone by Reagents Other than Mg + MgI_2.—The reduction of phenyl α-naphthyl ketone has been studied by a number of investigators.[6] Though many reducing agents were employed, only one method, that of Cohen using zinc and acetic acid, gave a pinacol. No directions, however, were given for carrying out this reduction. We dissolved 10 g. of phenyl a-naphthyl ketone in 175 cc. of cold glacial acetic acid and added 20 g. of zinc dust. After three days the mixture was diluted with water and the insoluble material was filtered off, washed with water and with alcohol. From the insoluble residue the pinacol was extracted by hot benzene. The pinacol obtained after evaporation of the benzene was recrystallized from a mixture of chloroform and alcohol and was obtained in the form of needles of melting point 158°; yield, 4.0 g. Our melting point, analysis and molecular weight were the same as those reported by Cohen for the pinacol. The presence of two hydroxyl groups in the compound was proved by its reaction with methylmagnesium iodide.

We found that the same substance is the product of the action of zinc and ammonium chloride on the ketone.

Rearrangement of the pinacol by warming with acetyl chloride or with acetic acid containing a trace of iodine gave a colorless solid which melted at 232° after it had been recrystallized from chloroformalcohol. The same compound resulted from the action of zinc and acetyl chloride on phenyl α-naphthyl ketone, a method that usually reduces a ketone to the pinacolin.[7]

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.88; H, 5.34. Mol. wt., calcd.: 448. Found: 449.

Unlike a pinacolin, the compound is very resistant to hot alcoholic potassium hydroxide. Even after thirty-six hours of boiling with a saturated solution of potassium hydroxide in alcohol, 70% of the compound was recovered unchanged.

Conversion of the Low-Melting Pinacol into the High-Melting Pinacol.—A benzene solution of 2.0 g. of the low-melting pinacol (158°) was added to a filtered ethereal solution of ethylmagnesium iodide. A vigorous evolution of ethane took place and the solution of the pinacolate became dark green in color. The bottle was stoppered and allowed to stand for twenty-four hours at room temperature. The solution was then

---

[5] Ref. 2, p. 246

[6] Lehne and Caille, *Ber.*, **13**, 359 (1880); Beckmann and Paul, *Ann.*, 266, 10 (1891); Elbs, *J. prakt. Chem.*, (2) *35*, 504 (1887); Elbs and Brand, *Z. Elektrochem.*, 8, 785 (1902); Cohen, *Rec. trav. chim.*, **38**, 80, 120 (1919); Montagne, *ibid.*, 27, 359 (1908).

[7] Zagoumenny, Bull. *soc. chim.*, (2) *34*, 329 (1880); J. Russ. *Phys.-Chem. Soc.*, *12*, *426* (1880).

decomposed with ice and ammonium chloride in the usual manner. The pinacol was recrystallized and was obtained now in the form of prisms having the melting point 215–217°. This new pinacol was found to be identical with the pinacol produced by reduction of the ketone by Mg + MgI_2. For further verification the pinacol was treated with hot acetic acid containing iodine, whereupon the expected pinacolin of melting point 216° resulted.

Reduction of Phenyl β-Naphthyl Ketone

Diphenyl-di-β-naphthyl Pinacol.—2.32 g. of phenyl-β-naphthyl ketone was reduced by 1.0 g. of magnesium and 3.0 g. of magnesium iodide in 30 cc. of ether–benzene (1:1). During the process of reduction the solution became reddish brown in color. This color was instantly destroyed when the solution came in contact with oxygen of the air, but it was restored when the air was prevented from entering. The loss of magnesium corresponded to 105% of the theoretical value and the magnesium hydroxide produced on hydrolysis was equivalent to 102%. The crude pinacol was recrystallized from chloroform–alcohol and was obtained in the form of needles; m. p. 175°; yield of pure pinacol, 91%.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 86.90; H, 5.68. Mol. wt., calcd.: 466. Found: 461.

An identical pinacol resulted from the reduction of the ketone by zinc and acetic acid.

A quantitative yield of the pinacolin $(C_6H_5)(C_{10}H_7)_2CCO(C_6H_5)$, resulted on dehydration of the pinacol. After being recrystallized from a mixture of benzene and acetic acid, the pinacolin melted at 181–182°.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.83; H, 5.24. Mol. wt., calcd.: 448. Found: 450.

One-half gram of this pinacolin heated with alcoholic potassium hydroxide for six hours gave 0.130 g. (96%) of benzoic acid.

Summary

Both phenyl α-naphthyl ketone and phenyl β-naphthyl ketone are reduced by the binary system, Mg + MgI_2 to ketyls, RR′C—OMgI, which associate to pinacolates, RR′C(OMgI)(IMgO)CRR′. Hydrolysis of the pinacolates gives the corresponding pinacols.

On rearrangement of the pinacols to the pinacolins, the naphthyl group wanders in preference to the phenyl group.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF PRINCETON UNIVERSITY]

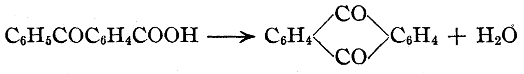
A STUDY OF THE DEHYDRATION OF ORTHO-BENZOYLBENZOIC ACID

BY A. H. GLEASON AND GREGG DOUGHERTY

RECEIVED OCTOBER 1, 1928 PUBLISHED JANUARY 8, 1929

Introduction

It was first noted by Liebermann[1] that anthraquinone could be formed by the elimination of water from o-benzoylbenzoic acid.



$$C_6H_5COC_6H_4COOH \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4 + H_2O$$

This process has come to have considerable technical importance because it is the principal step in the manufacture of synthetic anthraquinone. In addition, the reaction has certain unusual features which make it interesting from a purely theoretical point of view. For example, it is one of the few condensation reactions involving the use of strong dehydrating reagents such as sulfuric acid in which the yields are very high and side reactions negligible. In fact, under the proper conditions, o-benzoylbenzoic acid is converted apparently quantitatively into anthraquinone. This reaction should lend itself well to kinetic studies which might throw light on the mechanism of such processes in general.

In the synthetic method for producing o-benzoylbenzoic acid from phthalic anhydride and benzene in the presence of aluminum chloride, it is possible, by using substitution products of benzene and the anhydride, to prepare various substituted o-benzoylbenzoic acids which in turn can be condensed to the corresponding anthraquinones. This would seem to be a convenient way, therefore, of ascertaining the influence of different substituents in the benzene ring on this type of reaction. It has been our purpose, first to make a general study of the transformation using the unsubstituted acid, and then to attempt measurements showing the influence of substituents on the rate of reaction. The results of the first investigation are given in this paper.

The Dehydration of o-Benzoylbenzoic Acid under Various Conditions.—It has been found that the acid, when heated alone, yields small amounts of anthraquinone; the reaction temperature is quite high, 220°, and numerous by-products are formed, among them benzophenone.[2] Catalysts such as aluminum chloride, the sulfates of mercury, copper, tin, magnesium and silver and other anhydrous salts which might be expected to accelerate this type of reaction had little or no effect. Thallium chloride, however, had a marked influence on the reaction temperature and, in the

---

[1] Liebermann, *Ber.*, 7, 805 (1874).

[2] Dougherty, THIS JOURNAL, 50, 571 (1928).

presence of traces of this salt, a strong positive test for anthraquinone was obtained at 180°.

It is known that phosphorus pentoxide will cause this condensation,[3] but the yields are not good. With meta- and pyrophosphoric acids the yield of anthraquinone is negligible even with prolonged heating at 100°. The o-benzoylbenzoic acid dissolves very slowly in these acids and hence would make accurate velocity measurements difficult even if the acids were good condensing agents.

Concentrated sulfuric acid proved to be a better condensing agent than the literature implied. That is, most preparation directions for forming anthraquinone from o-benzoylbenzoic acid call for fuming sulfuric acid. It was found that a solution containing ten parts of concentrated sulfuric acid to one of pure o-benzoylbenzoic acid gave a quantitative yield of anthraquinone when heated for two hours at 100°. Even at room temperature the reaction proceeds at a measurable rate with a yield of approximately 4% of the theoretical in one hundred hours. The addition of contact agents such as metallic sulfates to the sulfuric acid reaction mixture had no apparent effect on the rate of condensation. It would seem, from our experiments, that sulfuric acid is almost a specific in this condensation, and while o-benzoylbenzoic acid can be dehydrated by other means, side reactions occur and the yields are never good.

Reaction Velocity Measurements.—When solutions of one part of *o*-benzoylbenzoic acid and ten parts of 96% sulfuric acid were heated for varying lengths of time at a definite temperature, and the resulting amounts of anthraquinone determined (see Experimental Part), the rate of conversion, calculated as a monomolecular reaction, was found to give a good constant over the whole range.

t, hours	6	8	10	12	17	20	22	26	30	36
K at 65°	0.076	0.075	0.078	0.074	0.079	0.074	0.076	0.076	0.078	0.076

t, hours	2	3	4	5	6	7	8	10	12	15
K at 75°	0.242	0.257	0.272	0.255	0.256	0.263	0 256	0.272	0.256	0.272

The velocity constant at 85° was 0.838 and at higher temperatures the reaction was so rapid that accurate measurements could not be made by the method employed. It may be noted that the velocity constant is more than tripled for a 10° rise in temperature. These are rather remarkable results in view of the fact that water is eliminated during the reaction as the sulfuric acid is diluted. Frequently, reactions which proceed in the presence of sulfuric acid are markedly retarded when even small amounts of water are added, as the negative catalytic effect increases exponentially. This is true of the decomposition of oxalic acid by sulfuric acid, and has been explained[4] by the assumption that the

---

[3] Behr *and van* Dorp, *Ber.*, 7,578 (1874).

[4] Bredig *and* Lichty, *J. Phys.* Chem., 11, 225 (1907).

reaction is dependent on the preliminary formation of an addition compound of sulfuric and oxalic acid; the addition of water results in a diminution in the amount of this complex formed.[5]

Since in the oxalic acid decomposition an addition of 0.05% of water, added at 25°, reduces the speed of reaction to one-sixth of that when no water is present, it would appear probable that the o-benzoylbenzoic acid condensation differs fundamentally from reactions of the oxalic acid type.

It might be thought that a monomolecular constant was obtained simply because an excess of the condensing agent was used, but experiments using much smaller ratios of reactant to condensing agent, down to 1:6, gave a good constant (K = 0.238, average deviation 1%, at 75°). When acids (sulfuric) of strength varying from 86–96% were used in the condensation, constants were also obtained. The results from runs with different acid concentrations were compared by plotting the amount of anthraquinone produced in a given time against acid concentration. It may be seen from Curve I, which is a straight line within the experimental error, that the condensing power of the acid solution is directly proportional to the sulfuric acid content. The conclusions to be drawn from these experiments are: the one molecule of water produced during the formation of anthraquinone from o-benzoylbenzoic acid has little or no retarding effect on the reaction velocity and does not cause deviation from the monomolecular order as the reaction proceeds; water added to the sulfuric acid does have a retarding action and in direct proportion to the amount added, but the effect is not as great as in reactions of the oxalic acid type.

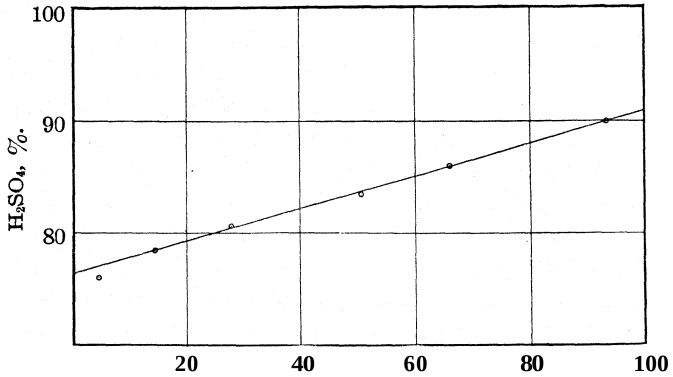


Fig. 1.—Theoretical yield when heated for 4 hours at 75°, %.

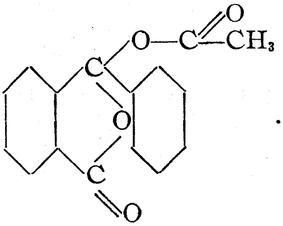
Formation of Anthraquinone from Esters and Acyl Derivatives.—It has been found that esters of o-benzoylbenzoic acid, which presumably have the formula $C_6H_5COC_6H_4COOR$, may be condensed by

---

[5] Taylor, *J. Phys. Chem.*, 27, 322 (1923).

sulfuric acid to anthraquinone, and in the ease of the methyl, ethyl and *iso*propyl compounds the reaction is clean-cut and the yields are nearly as high as with the free o-benzoylbenzoic acid. Here, of course, the alcohols are eliminated instead of water. With esters containing alkyl groups of higher carbon content the reaction is complicated by the formation of unidentified by-products and the yields are not good. This is true of the normal butyl ester, which is a viscous liquid.

When equimolecular quantities of the methyl, ethyl and isopropyl esters are treated with concentrated sulfuric acid under the same conditions, the yields of anthraquinone are almost identical, but are smaller than with the free o-benzoylbenzoic acid: methyl ester 1.25 g., ethyl ester 1.23 g., isopropyl ester 1.28 g. of anthraquinone. Apparently the velocity of the ester reaction is independent of the particular alkyl group present and lower than that of the free acid due to a reaction between the alcohol and sulfuric acid which diminishes the concentration of the latter.

o-Benzoylbenzoic acid may be acylated, and it undoubtedly reacts with acetylating reagents in the enolic form, so that the structure of the acetyl derivative is 

. It was interesting to find out whether this compound could be condensed to anthraquinone and to compare the rate of the reaction with that of the free acid and the esters. The results indicated that the condensation took place with even greater ease than that of the esters and, in fact, is comparable with that of the free acid: acetyl derivative 1.40 g., o-benzoylbenzoic acid, 1.39 g. of anthraquinone. It was previously determined that glacial acetic acid and acetic anhydride did not effect the condensation of o-benzoylbenzoic acid.

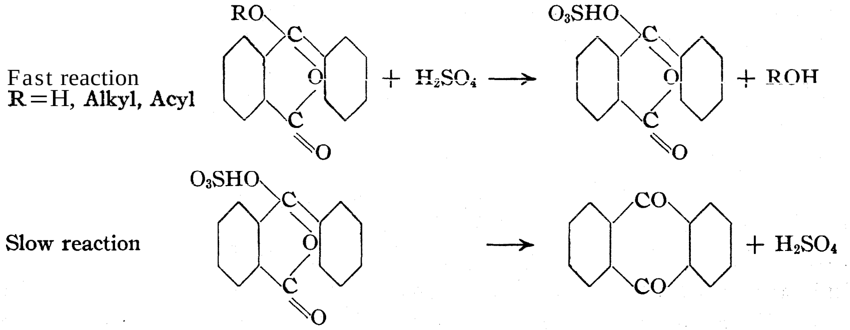
Mechanism of the Reaction.—In order to account for the fact that this condensation, under our experimental conditions, gives a constant for a monomolecular reaction over the whole range, we must either assume an hypothesis in which two opposite effects just balance each other and the results are more or less due to chance, or that the reaction proceeds in such a way that all of the water is eliminated at the start and rapidly as compared to the subsequent reaction which we measure. As regards the first possibility, Francis,[6] from a study of certain ionic reactions, concludes that "the reactivity of a dissolved substance is increased by a change in environment in a direction which will tend to throw it out of solution." We have this condition in the o-benzoylbenzoic acid con-

---

Francis, THIS JOURNAL, 48,662 (1926).

densation: water is eliminated and the solubility of the organic acid is appreciably lowered. On the other hand, the water dilutes the sulfuric acid and diminishes its efficiency as a condensing agent. In order that a monomolecular curve may be obtained, based on the concentration of the o-benzoylbenzoic acid, it is necessary that these two opposing effects be equal. It seems to us unlikely that such an explanation is the true one and we are inclined to believe that our experimental results point to a somewhat less complicated mechanism.

The similarity in the rates of condensation of the three esters indicates that the actual elimination of alcohol is not the reaction which is measured but that the o-benzoylbenzoic acid ester first reacts rapidly with the sulfuric acid and afterwards there is a slow decomposition of the resulting compound. It would seem probable that the free o-benzoylbenzoic acid behaves similarly. The equality of rates when the free acid and the acetyl derivative are condensed points to the same thing and suggests further that the two are in the same tautomeric condition during the reaction, that is, in the enolic form. The steps in the process are indicated by the following equations:



The elimination of water during the fast reaction explains why it has no retarding effect in the process as measured, although when water is actually added to the sulfuric acid beforehand, the rate is lowered. However, the formation of sulfuric acid during the slow reaction would seem to reverse the difficulty since the increased acid concentration should accelerate the reaction. That it does not do so may be explained by the formation of an addition compound of one molecule of sulfuric acid and one of anthraquinone, which prevents the acid eliminated from being effective in the condensation. There is ample evidence for the formation of such addition complexes between concentrated sulfuric acid and organic compounds containing oxygen.[7]

An attempt was made to show directly by the freezing-point method the existence of the addition compound. This was not successful due to

---

[7] Kendall and Carpenter, THIS JOURNAL, 36, **2498** (1914).

the fact that at the high melting points encountered, with even moderate concentrations of anthraquinone, there was decomposition and probably sulfonation. The formation of addition compounds is used frequently to explain reactivity, but in this case there is no appreciable reverse reaction and the only effect of the addition compound is to prevent the eliminated sulfuric acid from functioning as a condensing agent.

Experimental Part

For the qualitative determination of anthraquinone the anthraquinol test was used: heating with zinc dust and dilute sodium hydroxide solution produces a red color. In the preliminary experiments the depth of color was used as a rough estimation of the amount formed.

In determining the anthraquinone quantitatively use was made of the fact that it is insoluble in water and sodium hydroxide solution, while the o-benzoylbenzoic acid is soluble both in hot water and alkali solutions. The reaction mixtures, contained in large test-tubes fitted with rubber stoppers and calcium chloride tubes, were heated in a constant-temperature bath for definite lengths of time. The solutions were poured into cold water, stirred, heated to 80–90° and allowed to settle for five minutes. The more or less clear liquid was decanted off through a small Büchner funnel. To the precipitate in the beaker 2 N sodium hydroxide solution was added to definite alkalinity, the mixture was stirred and warmed and the precipitate collected on the funnel used above. After washing with hot water until the washings gave a neutral reaction with litmus, the anthraquinone was dried on the funnel for four hours at 110°. It was finally carefully removed to a clock glass, dried and weighed to constant weight. The average experimental error was less than 1%.

Summary

Attempts have been made to form anthraquinone by the elimination of water from o-benzoylbenzoic acid by various methods.

The reaction in which-sulfuric acid is used as the condensing agent has been studied, and an explanation of the mechanism of this type of reaction has been offered.

It has been found that the esters and acyl derivatives of *o*-benzoylbenzoic acid form anthraquinone under the same conditions as the free acid.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, NO. 46]

DIRECT SUBSTITUTION ON THE NITROGEN OF 5,5-DIALKYLBARBITURIC ACIDS

BY ARTHUR W. DOX AND EDWARD G. JONES

RECEIVED OCTOBER 8, 1928 PUBLISHED JANUARY 8, 1929

On account of the high dissociation constant of barbituric acid as compared with that of the 5,5-dialkylbarbituric acids, Wood and Anderson[1] concluded that the unsubstituted barbituric acid exists in solution in the tautomeric enol form representing a migration of hydrogen from the methylene to an adjacent carbonyl. As a further proof of this structure they synthesized the sodium salt of barbituric acid from ureidomalonamide and sodium hydroxide, the reaction, according to their view, consisting in hydrolysis of the amide with formation of a sodium salt, migration of a hydrogen from the methylene to carboxyl and ring closure with loss of water.

If, however, the sodium salt of barbituric acid is actually the enolic form, as postulated by Wood and Anderson, it is rather surprising that alkyl derivatives prepared therefrom are not known to occur in this form. Treatment of sodium barbiturate with alkyl halides yields apparently only derivatives in which alkyl has replaced the methylene hydrogen. Thus, 5-allyl- and 5,5-diallylbarbituric acids may be prepared from barbituric acid and allyl bromide in the presence of sodium acetate.[2] Since barbituric acid is a stronger acid than acetic, it may be assumed that sodium barbiturate is first formed in this reaction. A somewhat more direct reaction is described by Volwiler,[3] where n-butylallylbarbituric acid is prepared from allyl bromide and the sodium salt of *n*-butylbarbituric acid. The less reactive alkyl halides, *e.* g., ethyl bromide, however, give a poor yield of alkylbarbituric acids, and the preparation of such derivatives by direct alkylation has not been developed commercially. All derivatives thus far prepared in this way are identical with the corresponding derivatives prepared by condensation of alkylmalonic esters with urea; that is, the tautomeric alkyl derivatives of barbituric acid are not known.

Further substitution to yield tri- and tetra-alkylbarbituric acids has not hitherto been performed by direct alkylation. Fischer and Dilthey[4] prepared N-methyl- and N-phenyldiethylbarbituric acids by condensation of ethyl diethylmalonate with methylurea and phenylurea, respectively, and tetra-ethylbarbituric acid from diethylmalonyl chloride and

---

[1] Wood and Anderson, J. Chem. *Soc.*, 95, 979 (1909).

[2] Preiswerk and Grether, U. S. Patent 1,042,265 (1912).

[3] Volwiler, U. S. Patent 1,636,201 (1927).

[4] Fischer and Dilthey, Ann., 335, 334 (1904).

sym.-diethylurea. The series of 1,5,5-trialkylbarbituric acids was recently extended by Dox and Hjort[5] and that of 1-aryl-5,5-dialkylbarbituric acids by Hjort and Dox.[6] All of these derivatives were obtained by condensation of the ethyl dialkylmalonate with the appropriate alkyl- or arylurea.

In view of the ease with which the 5,5-dialkylbarbituric acids react with p-nitrobenzyl chloride in the presence of alkali, as shown by Lyons and Dox,[7] to give further substitution on one or both of the imide hydrogens, it seemed probable that other reactive halides might yield analogous products. Here the possibility of tautomeric forms again arises, since the imide groupings are adjacent to carbonyls and the alkali salts of 5,5-dialkylbarbituric acids are believed by some to exist in the enolic form. The question of tautomerism was definitely disposed of in the case of 1-benzyl-5,5-diethylbarbituric acid. This derivative was prepared by both methods, *viz.*, direct benzylation of sodium veronal and condensation of ethyl diethylmalonate with benzylurea. Both products were identical.

Alkylation on the nitrogen apparently does not occur until both methylene hydrogens have been substituted. For example, we treated the sodium salt of isopropylbarbituric acid with the molecular equivalent of benzyl chloride and obtained an isopropylbenzylbarbituric acid identical with that prepared by Dox and Yoder[8] from ethyl isopropylbenzylmalonate and urea. Both products melted at 229°.

The method used in preparing N-substituted derivatives of 5,5-dialkylbarbituric acids consisted simply in dissolving the dialkylbarbituric acid in one equivalent of normal sodium hydroxide and refluxing for several hours with one equivalent of the alkyl halide. The halides used in this work were benzyl chloride and allyl bromide. The product in most cases separated as an oil which became crystalline on standing overnight. Occasionally a by-product insoluble in alkali was obtained which had the properties of a dialkylacetylurea. This is known to result from certain dialkylbarbituric acids when treated with alkali, the reaction consisting in hydrolysis of the pyrimidine ring and loss of carbon dioxide The trisubstituted barbituric acids invariably melted lower than the parent dialkylbarbituric acid. They were purified by recrystallization from dilute alcohol or by acidifying the solution in dilute alkali.

In the following table eight such derivatives are described.

The purification of the trialkylbarbituric acid thus formed involves a fractional crystallization. Even though molecular proportions of the

---

[5] Dox and Hjort, J. *Pharmacol.*, 31, 455 (1927).

[6] Hjort and Dox, unpublished **data.**

[7] Lyons and Dox, THIS JOURNAL, 51,288 (1929).

[8] Dox and Yoder, *ibid.*, 44, 1144 (1922).

TABLE I

BARBITURIC ACID DERIVATIVES

N-Benzyl deriv. of	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Diethylbarbituric acid	127	10.22	10.19, 10.24
Ethyl iso-amylbarbituric acid	90	8.88	8.96, 8.97
Ethylphenylbarbituric acid	113	8.69	8.48, 8.66
Diallylbarbituric acid	116	9.39	9.29, ...
Allyl *sec.*-butylbarbituric acid	90–91	8.92	9.13, 9.14
N-Allyl deriv. of			
Diethylbarbituric acid	75	12.50	12.66, 12.61
Diallylbarbituric acid	68–69	11.29	11.40, 11.38
Dipropylbarbituric acid	73	11.11	10.90, 10.71

reactants are used, some tetra-alkyl derivative is simultaneously formed and a corresponding amount of the original substance remains unreacted. The former is readily removed by means of its insolubility in dilute alkali, but for the separation of tri- and dialkylbarbituric acids several crystallizations are necessary. In only one case was the tetra-alkyl derivative isolated and identified, *viz.*, diallyldipropylbarbituric acid, which melted at 62–63°; N found, 9.50, calcd., 9.59.

Summary

The sodium salts of 5,5-dialkylbarbituric acids react with such halides as benzyl chloride and allyl bromide to give further substitution on the nitrogen. A trialkyl- or even a tetra-alkylbarbituric acid can thus be obtained. This further substitution results in a marked lowering of the melting point.

DETROIT, MICHIGAN

NEW BOOKS

The Physics of Crystals. By ABRAM F. JOFFE, Ph.D., D.Sc., D.Eng., LL.D., Director, Roentgen Institute; Director, Physical Technical Institute, Leningrad, Russia. Edited by Leonard B. Loeb, Associate Professor of Physics in the University of California. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City, 1928. xi + 198 pp. 61 figs. 15 X 23.5 cm. Price $3.00.

When the reviewer first read the publisher's announcement of this book he was at once prejudiced against it. The story in that announcement of the way in which the author's results had first been treated looked too much like the efforts of a newspaper sob-reporter. After having studied the book (it deserves study, not merely reading), the reviewer's prejudice has been entirely overcome and he has even pasted the publisher's announcement on the flyleaf as a permanent record of some of the difficulties which the author overcame.

The first two chapters give a highly compressed account of the electrical theory of crystal lattices. After these two introductory chapters the author takes up in fifteen chapters the investigations of himself and his staff on the mechanical and electrical properties of crystals. These experiments show such unusual ingenuity and skill that many of them make as fascinating reading as a detective story. He shows that elastic after-effect, and elastic fatigue are properties of polycrystal materials, but are absent in single crystals; he explains clearly what goes on when a crystal is permanently deformed (as in plastic flow of solids); he accounts satisfactorily for the discrepancy between the values of tensile strength as calculated from crystal theory and the values ordinarily found by experiment. He proves that even the crystals of insulating substances like quartz obey Ohm's Law if only polarization is taken into account. It appears that ordinary "pure" individual crystals of insulators have specific conductivities which differ considerably from specimen to specimen, and extreme precautions must be taken in purification to get successive crystals to give identical results. The conductivity increases about 10% per degree centigrade. Strangely enough no increase in conductivity is produced by the presence of water of crystallization. Faraday's laws of electrolysis were checked in solid crystals with an accuracy of 0.1%. The reviewer would interpret Joffe's results on electrolysis by saying that if an ionic crystal is composed of ions of considerably different packing radius, the only one to migrate appreciably in electrolysis at ordinary temperatures is the one with the smaller packing radius. The degree of dissociation in quartz is found (7×10^{14} at 17°) and the order of magnitude of mobility of the ions has been calculated (10^{-6} cm. per sec.). It is hard to think of ionization by collision in solids, but Professor Joffe not only makes it look plausible, but he goes further and discusses the distribution of space charges in crystals. In fact the gap between the electrical properties of gases and solids seems to be pretty well bridged. Dielectric losses are largely explained by Joule's law of heating. The book closes with some interesting speculations on the maximum possible electric field in a dielectric and a statement of the effects to be expected.

The book is worth more than a single edition. That the English of the first edition is as smooth as it is, is evidently due to the efforts of the editor. The reviewer offers the following suggestions, not in the spirit of criticism, but in the hope that they will not only smooth the path of readers of the present edition, but also help in the preparation of a second edition.

1. The bottom of p. 38 should be interpreted in terms of the middle of p. 45.
2. On the fifth line of p. 70, "of" should read "between."
3. On the fifth line of p. 78, "of" should read "with."
4. The thirteenth and fourteenth lines of p. 106 would be more easily understood if the phrase "or cells deprived of positive ions" were in parentheses.

5. The use of "especially true" in the eleventh line of p. 105 is unfortunate.

6. In most places in the book "crystal" means "crystal of rock salt." Unless the reader discovers this, he may interpret some statements as generalizations which appear to apply strictly to sodium chloride, and which apply to other crystals only by inference.

7. The figures would be more readily understood if they had titles. The lack of titles is especially disturbing in Pig. 17 (p. 41) where the reader is left in doubt as to Curve IV until pp. 56 and 58, and where no explanation is given of squares, circles and crosses. Fig. 26 (p. 61) is a plot of log π against log S. The reader must infer from the text what these symbols mean, for they are nowhere explicitly defined. In Fig. 34 (p. 103), no explanation is given of the dots and circles. Apparently they merely serve to distinguish between curves. If so, it would have been easier for the reader if one curve had been full-line and the other dotted.

8. On p. **33** reference is made to an expansion which was said to have been made in a previous chapter in a series in Δr. The ordinary reader would appreciate a more adequate preparation for this statement.

9. Some of the equations are not accompanied by an adequate explanation of symbols. On p. 54, E and α are not defined. Equations 33 and 34 (p. 110) evidently follow the custom of using t for °C. and T for °K., but the fact is not so stated.

10. At the bottom of p. 33, $f_0' Ar$ should read $f' Ar$.

11. In Equation **32** (p. 109), σ^{100} should read σ_0^{100}.

WHEELER P. DAVEY

Organische Chemie. (Organic Chemistry.) By Prof. CARL OPPENHEIMER, Dr. Phil. et Med. (Berlin). Second, revised edition. Georg Thieme, Leipzig, Germany, 1928. xiv + 471 pp. 7 **figs.** 17 × 24.5 cm.

The chief novelty of this work is that the author has sought not only to present a clear and interesting account of the principles of organic chemistry, but to indicate the applications and extensions of this subject to the neighboring field of biology and to technology. The book is addressed to two groups: to those who are already fairly well grounded in the principles of organic chemistry as a pure science but who seek a first, orienting survey of the intensely interesting applications of the science to the study of life processes, and, secondly, to those specialists in fields other than that of organic chemistry who desire a comprehensive account of the present status of this subject. It is thus designed for the use of advanced readers.

The first six chapters, covering 93 pages, are devoted to a thorough and critical exposition of the general characteristics of the compounds of carbon, and of the modern theoretical conceptions regarding their reactions and properties. This is followed by a special part in which representatives of the different types of compounds are described. In this part of the book the author gives particular attention to the physiology and pharmacology of the substances and to their technical preparation and uses wherever the opportunity arises, The average organic chemist will find in these sections, and in the interesting descriptions of some of the more important biochemical processes, a wealth of information and a suggestive presentation of theory. The carbohydrates, the proteins and the alkaloids are treated more comprehensively than in most textbooks of organic chemistry, and one finds, in addition to the usual chapters, sections dealing with the relationship between structure and pharmacological action, chemotherapy, depsides, tannins, polyterpenes, sterols and bile acids, blood and leaf dyestuffs, ferments, antigens.

This second edition will be valued particularly for the inclusion of a large amount of work completed within the last few years. It may be noted, by way of example, that some account is given of the recent contributions to stereochemical theory of Weissenberg, Wohl and Freudenberg, Fajans, Kuhn, Ruzicka, Hückel and of Levene, of the views of the different German investigators in the field of the polysaccharides, of the investigations of Windaus on ergosterol, of Hans Fischer's porphyrin syntheses, of Scheibler's studies of bivalent carbon compounds, of Warburg's work on the respiration ferment. Furthermore, the author makes repeated use of the important Werner-Pfeiffer conception of the nature of complex compounds, and of the extensions to this general theory which we owe to Hantzsch and to Dilthey. The possibility of applying these new ideas to a wide variety of phenomena has been suggested throughout the book. Wieland's theory of the nature of oxidation processes likewise receives considerable attention. Dr. Oppenheimer, in addition to his wide experience in biochemistry, is thus in close touch with modern organic chemical theory, and he has written with enthusiasm a book which is highly useful and stimulating.

While the reviewer considers that the merits of this unusual text far outweigh the faults, he would like to call attention to certain shortcomings from the point of view of the organic chemist. It should be realized that the book is not well suited to the needs of the student who seeks to predict the properties of an unknown compound, or to devise a suitable method for its preparation. Thus one fails to find a statement regarding the directive influence of substituents in the benzene ring, and little is said regarding the effect of one group on the reactivity of other groups. β-Hydroxypropionic acid is dismissed with the remark that "(sie) kommt biologisch nicht vor und bietet kein weiteres Interesse." More serious than such omissions is the tendency of the author to adopt a too positive attitude with regard to debatable questions. It is stated, for example, that the C-alkylation of β-ketonic esters is dependent upon a tautomeric process, and no mention is made of the addition theory. Anthraquinone and phenanthrenequinone are regarded as entirely lacking in the properties of true quinones. The mechanism given for substitution in the benzene nucleus was probably intended to conform to the current theories, but the exposition is ambiguous and incorrect. The views of a large number of chemists have been disregarded in the failure even to mention the Erlenmeyer formula for naphthalene or the bridge-bond structure for anthracene.

Finally, it may be observed that the effort to condense the book by the liberal use of small type and abbreviations, and by omitting many important formulas and all references to the literature, appears somewhat unfortunate. The same object might have been achieved more happily had the author avoided the constant repetition of certain passages.

L. F. FIESER

Hormone und Innere Sekretion. (Hormones and Internal Secretions.) By FRITZ LAQUER, Lecturer at the University of Frankfort. Theodor Steinkopff, Dresden-Blasewitz, Germany, 1928. viii + 136 pages. 15.5 × 22 cm. Price, unbound, RM. 8.50; bound, RM. 10.

In the present plethora of monographs on the endocrine organs and hormones in health and disease, it is refreshing to read this little volume of Dr. Fritz Laquer because Dr. Laquer has succeeded in condensing the essential facts, biochemical, physiological and clinical, in a few pages with remarkable clearness, accuracy and critical judgment. No essential facts appear to be left out on any topic and wherever the author expresses his own judgment on controversial points this judgment appears unusually sound. In many cases, however, the individual authors' findings and conclusions are merely presented parallel with findings of opposite results. In separate chapters Dr. Laquer discusses the pancreas and insulin, the thyroid and thyroxin, the parathyroids, the hypophysis, the adrenals, the ovaries and testes and the thymus. In a final chapter the author briefly summarizes the claims and theories for endocrine functions and hormone character of other substances and organs such as pineal gland, choline, etc.

This little monograph by Dr. Fritz Laquer appears to be one of the briefest and at the same time most comprehensive, readable and reliable guides in the endocrine field in any language. 1218 separate literature references are given in connection with each subject under discussion.

A. J. CARLSON

The Journal of the American Chemical Society

VOL. 51 FEBRUARY, 1929 No. 2

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

HEAT CAPACITIES IN AQUEOUS SALT SOLUTIONS

BY MERLE RANDALL AND FREDERICK D. ROSSINI

RECEIVED JUNE 22, 1928 PUBLISHED FEBRUARY 5, 1929

Whenever two substances, A and B, are mixed together the heat capacity of the mixture will be the sum of the heat capacities of the separate substances if the temperature function of the energy state of A, and of B, is the same in the mixture as for each substance separately. It is possible also for their heat capacities to be additive if the deviation of the heat capacity of A, in going from the pure state into the mixture, is exactly negative that of B. If, however, molecules B exert some special influence upon molecules A, then their heat capacities usually will not be additive.

It has been known for a long time that the heat capacity of a given amount of water is greater than that of the same amount of water plus a small amount of any substance which is a strong electrolyte.[1] This behavior can be explained in the following manner. Suppose we have a system consisting of 1000 g. of water, whose heat capacity is G calories. If we add to this water one single molecule of sodium chloride we shall have a system consisting of 1000 g. of water, one sodium ion, and one chloride ion. The heat capacity of this system we find to be $(G - a)$ calories. Then $(-a)$ calories is, apparently, the heat capacity of one sodium ion plus one chloride ion. Since we are dealing with an infinitely dilute solution,[2] Φ° and also $\bar{C}_{p_2}^\circ$ for one gram mole of sodium ion plus one

---

[1] Thomsen, "Thermochemistry," Longmans Green and Co., London, 1908, p. 165, says, "When an aqueous solution is diluted with water the molecular heat of the solution formed is less than the sum of that of the original solution together with that of the water." This is true in every case only if the solute is a strong electrolyte. It is possible also that it is not always true for very concentrated solutions.

[2] The symbols which are pertinent to the main discussion of this paper are defined as follows: m, the molality, the number of moles of solute per 1000 g. (or 55.508 moles) of water *in vacuo*. C_p, the heat capacity of that amount of solution, of molality m, which contains 1000 g. of water plus m moles of solute. $\bar{C}_{p_2}$, the partial molal heat capacity of the solute. This is dC_p/dm, and is the change in the heat capacity of a very large amount of solution on the addition of 1 mole of solute. (Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co.,

gram mole of chloride ion equals $-a \times 6.06 \times 10^{23}$ cal. The presence of the two ions has so affected the water molecules that their heat capacity has been decreased by an amount equal to a calories plus the intrinsic heat capacity of one sodium ion and one chloride ion.

Methods of Determining and Calculating the Apparent and Partial Molal Heat Capacities and the Specific Heat

The method employed in this work to determine these quantities is to measure the difference in the heat capacity of the two systems, (A) 1000 g. of water (heat capacity is 55.508 $\bar{c}_{p_1}{}^\circ$); (B) 1000 g. of water plus m moles of salt (heat capacity is C_p). Then ΔC_p, the apparent heat capacity of the added salt, is given by the equation

$$\Delta C_p = C_p - 55.508\ \bar{c}_{p1}{}^\circ \qquad (1)$$

The apparent heat capacity of the added salt per mole of the added salt is

$$\Phi = \Delta C_p/m \qquad (2)$$

If Φ is plotted against $m^{1/2}$, as in Fig. 3, then

$$\bar{c}_{p2} = \Phi + {}^1/_2 m^{1/2}(\mathrm{d}\Phi/\mathrm{d}m^{1/2}) \qquad (3)$$

That this is true can be shown as follows. From Equations 1 and 2

$$\Phi = (C_p - 55.508\ \bar{c}_{p1}{}^\circ)/m \qquad (4)$$

Differentiating9 with respect to $m^{1/2}$, we find

$$\mathrm{d}\Phi/\mathrm{d}m^{1/2} = m(\mathrm{d}C_p/\mathrm{d}m^{1/2}) - (C_p - 55.508\ \bar{c}_{p1}{}^\circ)2m^{1/2}/m^2 \qquad (5)$$

But $C_p - 55.508\ \bar{c}_{p_1}{}^\circ = m\Phi$, and $m(\mathrm{d}C_p/\mathrm{d}m^{1/2}) = 2m^{3/2}(\mathrm{d}C_p/\mathrm{d}m) = 2m^{3/2}\bar{c}_{p_2}$. Making these substitutions and multiplying by ${}^1/_2 m^{1/2}$, we have Equation 3. Or, the partial molal heat capacity of the solute is equal to the apparent molal heat capacity plus ${}^1/_2$ the product of $m^{1/2}$ times the slope of the curve of Fig. 3.

When Φ and $\bar{c}_{p_2}$ are known, $\bar{c}_{p_1}$ can be calculated as follows.[2] By definition

$$C_p = m\bar{c}_{p2} + 55.508\ \bar{c}_{p1} \qquad (6)$$

then

$$\bar{c}_{p1} = (C_p - m\bar{c}_{p2})/55.508 \qquad (7)$$

From Equations 1 and 2

$$C_p = m\Phi + 55.508\ \bar{c}_{p1}{}^\circ \qquad (8)$$

Hence

$$\bar{c}_{p1} = (m\Phi + 55.508\ \bar{c}_{p1}{}^\circ - m\bar{c}_{p2})/55.508 = (m/55.508)(\Phi - \bar{c}_{p2}) + \bar{c}_{p1}{}^\circ \qquad (9)$$

The specific heat of 1 gram of a solution of molality m is

$$\text{Specific heat} = (m\Phi + 55.508\ \bar{c}_{p1}{}^\circ)/W \qquad (10)$$

New Pork, 1923, p. 83.) $\bar{c}_{p2}{}^\circ$, the value of $\bar{c}_{p2}$ when m is zero. $\bar{c}_{p1}$, the partial molal heat capacity of the water. This is the change in the heat capacity of a very large amount of solution on the addition of 1 mole of water. Specific heat, the heat capacity of one gram of solution. $\bar{c}_{p1}{}^\circ$, the value of $\bar{c}_{p1}$ when m is zero. Φ, the apparent molal heat capacity of the solute, is $(C_p - 55.508\ \bar{c}_{p1}{}^\circ)/m$. It is the change in heat capacity per mole of solute, caused by the addition of m moles of solute to 1000 g. of water. $\Phi^\circ = \bar{c}_{p2}{}^\circ$, the value of the apparent molal heat capacity at $m = 0$.

where W is the weight of the amount of solution which contains 1000 g. of solution.

From the foregoing it is seen how all the four quantities, Φ, $\bar{c}_{p_2}$, $\bar{c}_{p_1}$ and specific heat can be calculated if the ΔC_p of Equation 1 is measured.

In this investigation, the method suggested by Randall and Bisson[3] and used by Randall and Ramage[4] is employed: given two calorimeter units identically alike, and containing like resistance heating units connected in series.

Charge both Units 1 and 2 with the same amount of water, say 1000 g. Pass a current in series through the two units for such a time as to cause a temperature rise in Unit 1 of Δt_1. If Unit 2 were identically the same as Unit 1 in every respect, its temperature rise would also be Δt_1, but there will be some small physical difference between the two units, so that actually the temperature rise in Unit 2 will be $\Delta t_1 + \Delta t_2$, where Δt_2 is the difference in temperature rise between Units 1 and 2 and is very small compared with Δt_1. Now *m* moles of salt are added to Unit 2 and again a current is passed through Units 1 and 2 in series until the temperature rise in 1 is again Δt_1. The temperature rise in Unit 2 **will** now be $\Delta t_1 + \Delta t_2'$. The heat capacity of Unit 1 is the same for both runs; the same amount of electrical energy must have gone into Unit 1 in both runs. Since the two units are in series and have like heating resistances, the energy that has gone into Unit 2 is the same in both runs. Hence for Unit 2

$$(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O})(\Delta t_1 + \Delta t_2) = (C_p, \text{Unit } 2 + C_p, \text{solution})\,(\Delta t_1 + \text{At,'}) \qquad (11)$$

or

$$(\Delta t_1 + \Delta t_2)/(\Delta t_1 + \text{At,'}) = (C_p, \text{Unit } 2 + C_p, \text{solution})/(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O}) \qquad (12)$$

Subtracting one from both sides, we have

$$(\text{At,} - \Delta t_2')/(\Delta t_1 + \Delta t_2') = (C_p, \text{solution} - C_p, \text{H}_2\text{O})/(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O}) \qquad (13)$$

Hence

$$\Delta C_p = [(\Delta t_2 - \Delta t_2')/(\Delta t_1 + \Delta t_2')](C_p, \text{Unit } 2 + C_p\text{H}_2\text{O}) \qquad (14)$$

The Calorimeter

The calorimeter of Randall and Ramage[4] was rebuilt. A nickel-plated brass plate fitted the guide frame on the vertical runways of the thermostat case of Randall and Bisson.[3,4] This plate was laid out so that three nickel-plated brass cylinders A, 15 cm. X 27 cm., could be bolted to it from the lower side, and so that the three leg multiple thermel case would fit from above, one leg into each cylinder. Above each cylinder were sets of holes with extension tubes to provide for the entry of stirrer, heating coil leads and cooling coil leads. The 20-junction and 50-junction thermel of Randall and Bisson[3,4] and their mechanism for propelling the stirrers in the three units were slightly altered and used in this assembly.

As recommended by Randall and Ramage,[4] the Dewar flasks containing the water or solution were placed within cylinders and the whole assembly was submerged in the

---

[3] Randall and Bisson, This Journal, 42, 347 (1920).

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

oil-bath of the thermostat. In this manner the slight variation in the temperature of the oil-bath was ironed out before reaching the liquid in the Dewar flasks. The air in the enclosed space above the bath was always in temperature equilibrium with the oil.

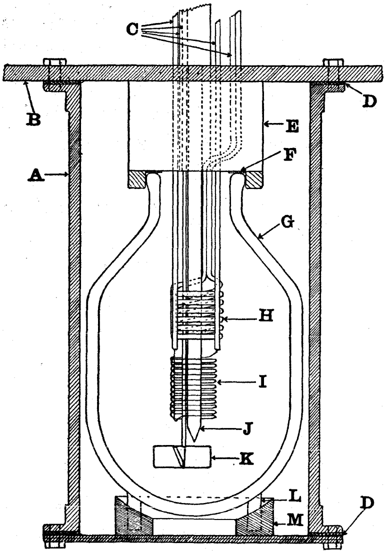


Fig. 1.—One unit of calorimeter.

A cross section of one of the three calorimeter units ($^2/_7$ of actual size) is shown in Pig. 1. The nickel-plated brass cylinder, **A,** was bolted to the nickel-plated brass main plate, B, with the various extension tubes, C, leading to above the surface of the oil in the bath. The gasket, D, made of Garlock sheet rubber packing was shellacked to the cylinder. The vacuum flask, G, was supported on the rubber pieces, L, which were held in the circular piece of balsa wood, M. The flask was tightly held against the rubber gasket, P, which was shellacked to the balsa wood block, E, through which run the stirrer, thermel, entry opening, heating coil leads and cooling coil leads. The protecting tube, J, of the copper-constantan thermel was of Pyrex glass. The cooling coil, H, was of 0.32 cm. copper tubing, joined to leads of thin-walled German silver tubing, and K was a three vane all glass stirrer with 0.3 cm. glass shaft, which was joined to the driving mechanism with rubber tubing.

The heating coil, I, was made by drawing fine silver tubing over double silk covered manganin resistance wire, having a thin coating of bakelite. This silver tubing was coiled and then joined to 0.32 cm German silver tubing leading out of the unit. A cross section of one of the tubing junctions of the heating coil is shown in Fig. 2. The silver tubing P, whose outside diameter was about, 0.064 cm., was tightly drawn over the No. 38 D.S.C. manganin resistance wire, Q. The double silk insulation, S,S,S, has a thin coating of bakelite. The small silver tubing, P, was soldered, R,E, to a larger piece of silver tubing, which in turn fitted snugly into a brass bushing, U, in the 0.32-cm. German silver tubing, V. The lead, T, was No. 28 copper, and the lead, W, was No. 24 copper wire.

This type of heating coil has a very low heat capacity and the interchange of heat between the resistance wire and the solution is very rapid. About 120 cm. of wire was used in the coil and its resistance was about 70 ohms. The first coils used were of No. 30 D.S.C. manganin wire and had a resistance of about 10 ohms. The heating unit was silver plated and then gold plated; the cooling unit was heavily gold plated.

A 10-junction thermel gave the difference in temperature between the bath and Unit 3; the 20-junction thermel gave the temperature difference between Units 1 and 3; while the 50-junction thermel showed the difference in temperature between Units 1 and 2.

When the entire calorimeter assembly was submerged, the extension tubes, C, extended about 2.5 cm. above the surface of the oil. In this manner every part of the calorimeter proper, including the multiple thermel case, was completely immersed in the constant temperature oil-bath. The thermel case was screwed to the main plate of the calorimeter with rubber as gasket material and then shellacked to prevent dissolution of the rubber.

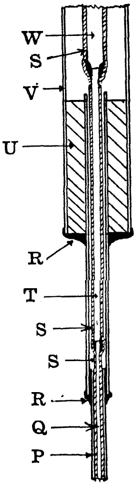


Fig. 2.—Detail of heating coil.

A Leeds and Northrup, White Double Potentiometer, with a range of 100,000 microvolts, and a Leeds and Northrup high sensitivity galvanometer were used to measure the potentials of the three thermels, the potential drop across and the current through the heating coils. These latter two were read only in the direct heat capacity runs.

To supply the working current in the potentiometer, two batteries of two each of Type B6H Edison alkaline cells were used. The entire electrical system was doubly shielded according to the recommendations of White.[5]

Calibration of the Apparatus

Two Meylan stop watches, for use in measuring the time in the direct heat capacity runs for determining the heat capacity of the flasks, were checked against the Observatory time signals and against the Howard Mean Time clock in the Observatory of the Astronomy Department. We thus found the factor (mean solar seconds) to be 1.0000 for the 0.2-sec. watch and 1.0002 for the 0.1-sec. watch.

Since the potential drop across the heating coils was much greater than the capacity of the potentiometer, a fraction $R_a/(R_a + R_b)$ was measured. The value of $(R_a + R_b)/R_a$, found by measuring the current through and the potential drop across known standard resistances, was 181.50, 181.50, 181.52, 181.50; mean 181.50.

The standard cell used for balancing the working current in the potentiometer was a saturated cell of the Weston type which was kept in the thermostat at 25.25°. The cell was placed in a metal can and the leads were brought out through a bakelite plate. The potential was checked against two new Weston and four new Eppley cells over the period of the investigation and was found to be 1.01808 ± 0.00002 v. at 25.25°. This agrees well with the value of 1.01807 v. calculated from the value 1.01830 v. for a saturated Weston cell at 20°, when corrected for the temperature difference.

The insulation resistances on all the thermels were checked and found to be greater than ten million ohms.

The energy current, furnished by lead storage batteries, was found to be non-fluctuating if the batteries were maintained at the proper charge.

The temperature of the oil in the thermostat was maintained at 25.25 ± 0.010°. The period of the fluctuations in the oil-bath temperature was from ten to eighteen minutes, depending upon the temperature of the room. The oil in the bath was kept well stirred with a four-vane, 8-cm. fan stirrer, running at about 630 r.p.m. Two special thermostat thermometers, which could be read to 0.005°, and which had been calibrated at the Bureau of Standards, were placed at different points in the oil-bath and indicated practically uniform temperature throughout the bath.

The high sensitivity galvanometer used was a Leeds and Northrup, Catalog No. 2285. with a period of six sec., an internal resistance of 37 ohms and an external critical damping resistance of 380 ohms. The galvanometer scale was placed 6.7 meters from the galvanometer, and with a telescope having a very high magnification one could estimate 0.2 mm. on the scale. Table I gives the approximate sensitivity of the galvanometer (in mm. on the scale) with the various thermels in the circuit.

TABLE I

SENSITIVITY OF GALVANOMETER

Thermel	10-Junction	20-Junction	50-Junction
Resistance of thermel, ohms	78.4	147	347
Sensitivity, mm. per mv.	40	30	18
Sensitivity, degrees per mm.	0.000057	0.000038	0.000025

---

[5] White, THIS JOURNAL, 36, 2011 (1914).

The 20-junction and the 50-junction thermel had been calibrated by Randall and Bisson[3] against a 4-junction thermel calibrated by the Bureau of Standards. Then the equation for the e.m.f. per junction was

$$\text{E.m.f.} = 40.8751 + 0.05075t^a - 0.0000613t^3 \qquad (15)$$

when one junction was at 0° and the other at a temperature of t°.

The e.m.f. produced on the thermel when one leg was at 0° and the other at the sodium sulfate triple point, 32.383°, was determined for all three thermels.

TABLE II

CALIBRATION OF THERMELS

Thermel	Measured e.m.f., microvolts	E.m.f. calcd. in microvolts	Ratio e.m.f. measured / e.m.f. calcd.
10-jc.	13,753.6	13,789.6	0.99738
20-jc.	27,504.3	27,579.1	.99729
50-jc.	68,759.9	68,947.8	.99727

The factors to be applied to the e.m.f.-temperature equation were 0.9973 for the 20- and the 50-junction thermels and 0.9974 for the 10-junction thermel. In this calibration the figures in the second column show the e.m.f. reading when it was constant to 0.3 microvolt for thirty minutes, with one leg in a mixture of clear cracked ice and conductivity water and the other in a solution of sodium sulfate in equilibrium with the two solid forms Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$, which has a temperatures of 32.383°. Conductivity water and thrice recrystallized sodium sulfate were used in making the solutions.

The optimum rate for the stirrers in the flasks was found to be 130 r.p.m. This produced good mixing of the water or the solution without developing an excessive amount of stirring energy. The stirring energy was found to be about 0.025 cal. per min. for the above rate with the stirrers used. This was determined by running the stirrers in Units 1 and 2 with the flasks containing water at the temperature of the bath. The only change in temperature occurring in the two flasks, 1 and 2, was then that due to evaporation and stirring. Readings on the 50-junction thermel joining these two flasks were taken for thirty minutes. Stirrer 2 was stopped for ten minutes and then again started. Then readings were again taken after equilibrium had been established. An extrapolation gave the reading which would have been found if Stirrer 2 had not been stopped. The difference in this and the actual observed reading was translated from microvolts to degrees to calories per minute by a simple calculation.

The heat leak from the bath into one of the vacuum flasks containing about 1200 g. of water was found to be about 10^{-5} cal. per sq. cm. per sec. per deg. This is an average for the entire surface of the Dewar flask, although actually most of this leak occurred through the thermel, stirrer, heating coil, and cooling coil leads. With the above amount of water in the vacuum flask, the heat flow into the flask (when its temperature was below that of the bath) from the bath was such as to cause a temperature rise in it of 0.00037 deg. per min. per deg. difference in temperature. Since at the start of an experiment the flask was 0.5° below the temperature of the bath, and was brought to the temperature of the bath in eight minutes, the total temperature rise due to the Newton flow of heat was $0.5 \times 8 \times 0.00037 = 0.00148°$, or about 0.003 of the total rise.

The stirring and evaporation difference between Flasks 1 and 2 as registered by the 50-junction thermel, and between Flasks 1 and 3, as registered by the 20-junction

---

[6] (a) Richards, Am. J. Sci., 6, 201 (1898); (b) Richards and Wells, *Proc.* Am. *Acad. Sci.*, 38,431 (1902); (c) Dickinson and Mueller, THIS JOURNAL, **29**, 1381 (1907).

thermel, varied slightly from run to run but was practically constant for a given run. Great precision in the determination of the stirring and evaporation difference between Flasks 1 and 2 was neoessary, and in most of the runs the stirring and evaporation difference was such as to cause a temperature difference in Units **1** and **2** of about 0.000010° per min. In some runs this was zero and in some as much as **0.000025**" per min.

Most of the stirring and evaporation difference between Flasks **1** and **2,** which is of great importance in a differential run, was due to a difference in evaporation from the two flasks. This evaporation was reduced by preventing gaseous connection between the inside of the flask and the air space between the flask and the cylinder. The only opening from the interior of the flask to the air space in the thermostat case was along the stirrer tube. This was reduced with some packing. **All** the other tubes were packed tightly. The 2.2 cm. cylindrical entry tube was neatly fitted with a removable cylinder of balsa wood.

The cooling of the calorimeters to the starting temperature, if they were above it. was accomplished by running compressed air, under a pressure of **0.5** atm. gage through coils of **0.6** cm. copper tubing immersed in liquid air and thence through rubber tubing to the cooling coil of a unit. The air from the exit tube of the cooling coil in each unit was discharged into the air above the bath. With this cooling system, each unit having *a* heat capacity when charged of about 1200 cal. could be cooled **0.5** deg. in about forty minutes. The moisture and carbon dioxide in the compressed air were removed with calcium chloride, soda lime and a liquid-air trap.

The lag of the rise in temperature of a solution, as registered by the e.m.f. of the thermel, behimd the electrical energy input was found to be about twenty-two seconds for an energy input of 75 cal. per min.

Heat Capacity of a Unit

By the capacity of a unit we shall mean the heat capacity of the vacuum flask plus the thermel, stirrer, heating unit and cooling unit within the flask.

Before any differential runs were made, the heat capacity of Unit **2** was determined. **A** weighed amount of water was placed in Flask **2** and brought to 24.75'. Units **1** and **3** contained water at 25.25°, the temperature of the bath. An amount of energy was put into Unit **2** such that its temperature rise was **0.5** deg. From the energy input and the temperature rise the heat capacity of the unit plus the contained water was calculated. The heat capacity of the unit alone was found by subtracting the heat capacity of the water.

In these direct heat capacity runs the heating time was made about 1000 sec. as the time was measured with a tenth-second stop watch. The energy input was found by taking the average value of potential times current over the period of the run (not the average value of potential times the average value of current) from appropriate plots of the observed value. The method of operation and method of calculation is indicated in Table III, which gives a condensed log of Run 19.

A plot of the temperature (in microvolts) of Unit **2** against the time during the run shows that from the tenth minute to the thirtieth minute

TABLE III

CONDENSED LOG OR RUN 19

C_p Unit 2 (Flask 387). 1:18 P.M., 8/10/27. 1244.62 X 1.00106 g. of water in 2. 1250 cc. of water in 1 and in 3. Energy time, 16 minutes and 12.8 seconds. Stirring rate, 135 r.p.m. Room temp., 21.4°. Bath temp., 25.25°.

Time		Reading		Time		Reading	
		Dial	Scale			Dial	Scale
0	50-jc.	1160	86.80[a]	21	50-jc.	410	67
2			85.00	22	P. D.	27670	63.2
4			83.00	23	Current	57850	89.0
6			81.10	24		57860	78.4
8			79.10	25	50-jc.	120	81
10[b]		1160	77.10[c]	26		60	64
				27[d]		20	77
11		1110	72	28		10	93.30
12	Current	57880	83.0	30		10	93.00[e]
13			82.2				
14			80.6	32			92.70[f]
15	P. D.	27680	66.0	34			92.50
16		27670	73.5	36			92.25
17	Current	57870	78.0	38			92.00
18			83.2	40			91.70
19	P. D.	27670	81.0	42			91.30
20			68.0	44			91.00[g]

[a] Zero, 84.65. [b] Energy on. [c] Zero, 84.65; e.m.f., 1155.80. [d] Energy off. [e] Zero, 84.40; sensitivity, 18.00 (50); e.m.f., 14.80. [f] Sensitivity, 29.90 (20). [g] Zero, 84.20.

Fore period, 50-jc., 0.97 cm./min. at 1158 microvolts. After period, 50-jc., 0.15 cm./min. at 1158 microvolts. U is the constant stirring and evaporation difference between Units 1 and 2. K is the heat leak constant.

$$1158\,K - U = 0.97 \qquad U = 0.15 \text{ cm./min.}$$
$$10\,K - U = 0.15$$
$$1148\,K = 0.82 \qquad K = 0.00071 \text{ cm./min./microvolt}$$

of the run Unit 2 was 9760 microvolt-minutes below the bath. Therefore the rise in temperature of Unit 2 during the run, due to the heat leak, was 9760 X 0.00071 = 6.90 cm. (scale deflection). The rise in temperature of Unit 2 due to the stirring and evaporation difference between Units 1 and 2 was 20 X 0.15 = 3.00 cm.

The total temperature rise not due to the energy input is then 6.90 + 3.00 or 9.90 cm., which is 5.50 microvolts. From the tenth minute to the thirtieth minute the actual temperature rise was 1155.80 − 14.80 or 1141.00 microvolts. The temperature rise due to the energy input alone was 1141.00 − 5.50 or 1135.50 microvolts, or 1135.50/(2165.8 × 0.9973) deg. The average input for the heating period, obtained by plotting the current and potential drop, was 0.016011 X 181.50 watts. The potential drop across the heating unit was obtained by multiplying the reading (P. D. in Table 111), in microvolts, by 181.50 and dividing by 10^6. The current is the reading (Current in Table III) of the potential drop in microvolts across a standard 0.1 ohm, multiplied by 10 and divided by 10^6. The time was 972.8 sec. The energy input = (972.8)(0.016011 X 181.50) – (0.9989) = 2823.10 joules. The factor correcting for the resistance of the leads to the heating unit is 0.9989. The total heat capacity is then 2823.10 × (2165.8 × 0.9973)/1135.50 = 5370.07 joules per deg. The heat capacity of the water at 25° is (1244.62)(1.00106) X 4.1728 = 5199.06 joules per deg., whence C_p for Unit 2 = 171.01 joules per deg., or 40.89 cal. per deg.

Runs 17, 18 and 19 gave 40.76, 40.96 and 40.89 cal. for the heat capacity of Unit 2, with Flask 387.

By making some differential runs, as explained in the next section, the change in the heat capacity of Unit 2 with volume of liquid was found to be as recorded in Table IV.

TABLE IV

CHANGE IN HEAT CAPACITY OF UNIT 2 (FLASK 387) WITH VOLUME OF SOLUTION

Vol. of liq., cc.	1180–1200	1200–1220	1220–1240	1240–1260	1260–1280	1280–1300
Change in C_p in cal./cc. (Unit 2)	0.005	0.006	0.007	0.008	0.009	0.010

These values were calculated from the results of eighteen runs.

The Differential Heat Capacity Run

The procedure followed in measuring ΔC_p was to charge Units 1 and 2 with water at 24.75' and Unit 3 at 25.25°, the temperature of the bath. An amount of energy sufficient to heat Units 1 and 2 to 25.25° was passed through the heating units in series. The temperature rise of Flask 2, $\Delta t_1 + \Delta t_2$, for a given temperature rise in Flask 1, Δt_1, was measured. Then Δn_2 moles of salt were added to Flask 2, and $\Delta t_1 + \Delta t_2$ was found for the rise of Δt_1 in Flask 1. In this way measurements of Δt_1 and Δt_2 were made after successive additions of salt and the ΔC_p between the original amount of water in Flask 2 and any given solution following it is

$$\Delta C_p(m) = (\Delta t_2(m = 0) - \Delta t_2(m))\,(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O})(m = 0)/(\Delta t_1 + \Delta t_2(m)) \quad (16)$$

The method of operation and of calculation is shown in Table V, which gives a condensed log of Run 64.

Materials, Constants, Molecular Weights, etc.

The salts used in this work were anhydrous C. P. samples thoroughly dried in an oven at 105°—Kahlbaum's sodium and potassium chlorides, and sodium and potassium nitrates; Merck's potassium sulfate; Baker and Adamson's sodium sulfate and bromide, and potassium bromide and Mallinckrodt's "Reagent Quality" potassium iodide.

The molality of a given solution is calculated from the weight of the water and the weight of the salt added. The water in the flask is weighed to 0.01 g. and the added salt to 0.001 g. All weighings are reduced to vacuum. The molecular weights of the salts are calculated from the International Atomic Weights for 1927.

The unit calorie was taken as the amount of energy required to raise the temperature of 1 g. of water from 15 to 16°. The ratio of the heat capacity of water at 25° to that

TABLE V

CONDENSED LOG OF DIFFERENTIAL RUN NO. 64

9:00 A.M., 12/13/27. 1250 cc. of water in Flask 1 and in 3. 1238.25 g. of water and 0.1005 moles of sodium chloride in Unit 2. Stirring rate, 115 r.p.m. Room temp., 21.0°. Bath temp., 25.25°.

Time		Reading Dial	 Scale	Time		Reading Dial	 Scale	Zero	Sensitivity
0	20-jc.	430	51.50	1	50-jc.	0	52.55	51.25	
4			48.90	5			52.70	51.30	
8			46.40	9			52.90	51.35	
12			43.90	13			53.10	51.35	
16		430	41.35	15			53.15	51.38	
17		390	69	16		0	53.20	51.40	
18		340	72						
23		90	73						
24		40	78						
25		0	66						
				31		0	51.45	51.40	
32		0	45.30	35			51.50	51.40	
36			44.80	39		0	51.60	51.40	17.80 (50)
40		0	44.20	43			51.55	51.30	
44			43.60	47			51.70	51.30	29.90 (20)
48			43.05	51			51.90	51.40	
52			42.50	55			52.05	51.35	
56			41.90						

Unit 1—Unit 3, 20-jc.		Unit 1—Unit 2, 50-jc.	
Fore period	−0.650 cm./min.	Fore period	0.032 cm./min.
After period	−0.138 cm./min.	After period	0.031 cm./min.

Stirring and evaporation, 24 × −0.138 = −3.31 cm. Total difference, 23 × 0.032 = 0.74 cm. Heat leak, 1900[(−0.650 − 0.138)/430] = −2.25 cm. Stirring, evaporation and leak, −5.56 cm. or −0.185 microvolts.

16th min.......	426.50	16th min.......	53.20 cm.
40th min......	−2.40	39th min.......	51.60 cm.
	428.90		1.60 cm.
	−1.85		0.74 cm.
	427.05		2.34 cm. or
Multiplying by 2.5000			
	1067.63		1.31 microvolts
$\Delta t_1 =$	1000.00 microvolts	$\Delta t_2 =$	1.23 microvolts

at 15.5° is taken from the data of Callendar and Barnes[7] to be 0.9979. The unit calorie is assumed to be equivalent to 4.182 joules.

Experimental Data

The experimental data are summarized in Table VI, in which Col. 1 gives the number of moles of salt added to the amount of water indicated

---

[7] See résumé of Lewis and Randall, ref. 2.

in the sub-heading of each section of the table; Col. 2 gives the molality of the solution; Cols. **3** and 4 give Δt_2 (in duplicate experiments), the temperature rise in microvolts of Unit 2 above Unit 1 for a rise of 1000 microvolts in Unit **1**; Col. 5 gives $\Delta t_2^\circ - \Delta t_2$ or the mean of the differences between Δt_2 for the runs when m is zero and the runs of the given molality; Col. *6* gives (ΔC_p) or the uncorrected change in heat capacity of the system due to the total added salt; Col. **7** the true ΔC_p of the system found by correcting the value of the previous column for the change in the heat capacity of the unit with the change of the volume of solution in the **flask** (see Table IV), and the last column the apparent molal heat capacity, Φ, which is found by dividing the value in Col. 7 by the molality. Two or more series of runs were made on each salt and the runs of different series are distinguished on the plots.

TABLE VI

APPARENT MOLAL HEAT CAPACITY OF SODIUM CHLORIDE[a]

1238.25 **g. water.** C_p **(Unit** 2) = 1275.8 **cal.**

Moles	m	Δt_2(I)	Δt_2(II)	Δt_2° − Ata	(ΔC_p)	ΔC_p	Φ
0.0	0.0	−0.20,	−0.26	0.0	0.0	0.0	
.0502	.0405	0.74,	0.53	−0.86	− 1.10	− 1.11	−22.1
.1005	.0812	1.21,	1.23	−1.47	− 1.87	− 1.89	−18.8
.2009	.1622	2.53,	2.63	− 281	− 3.57	− 3.61	−18.0
.3013	.2433	3.66,	3.71	−3.92	− 4.98	− 5.03	−16.7
.4266	.3445	4.82,	4.91	−5.10	− 6.47	− 6.55	−15.35
.5520	.4458	5.93,	5.85	−6.12	− 7.76	− 7.86	−14.25
.7023	.5671	6.82,	6.77	−7.03	− 8.91	− 9.04	−12.87
.8527	.6886	7.60,	7.70	−7.88	− 9.99	−10.15	−11.90
1.0030	,8100	8.32,	8.54	−8.66	−10.96	−11.15	−11.12
1.2036	.9720	8.84	..	−9.07	−11.47	−11.69	− 9.71
1.4042	1.1340	9.08	..	−9.31	−11.77	−12.03	− 8.57
1.6048	1.2958	9.27	..	−9.48	−11.98	−12.28	− 7.65
1.8054	1.4580	8.91	..	−9.14	−11.56	−11.90	− 6.59
2.0564	1.6607	8.17	..	−8.41	−10.64	−11.04	− 5.37
2.3074	1.8634	7.22	..	−7.45	− 9.44	− 9.89	− 4.29
2.5583	2.0660	5.71	..	−5.94	− 7.54	− 8.04	− 3.14
2.8093	2.2687	4.27,	4.28	−4.50	− 5.72	− 6.27	− 2.23
1192.96 g. **of water.** C_p **(Unit** 2) = 1230.6 **cal.**							
0.0	0.0	0.87,	0.75	0.0	0.0	0.0	0.0
2.2205	1.8613	8.00,	8.13	−7.26	− 8.87	− 9.12	− 4.11
2.7393	2.2961	4.96,	..	−4.15	− 5.08	− 5.43	− 1.98

[a] **Similar data for the other salts worked with may be found in a manuscript thesis by the Junior Author, filed in the University of California Library, May,** 1928.

The rounded values of the apparent molal heat capacity for the usual rounded values of m are given in the third column of Table VII. The values of the partial molal heat capacity of the solute calculated by means of the plots of Figs. **3** and 4 and the method of Equation **3,** are found in Col. 4. The values of the partial molal heat capacity of the water calculated by means of Equation 9 are given in Col. 5, and the specific heat of the solution referred to water as 0.9979 is calculated according to Equation 10 and is given in the last column.

Table VII

Rounded Values of Φ, $\bar{c}_{p2}$, $\bar{c}_{p1}$ and Specific Heat at 25° in Calories

m	Φ	$\bar{c}_{p2}$	$\bar{c}_{p1}$	Sp. ht.
Sodium Chloride				
0.00	−23.30	−23.30	17.9776	0.9979
.01	−22.05	−21.40	17.9774	.9971
.02	−21.55	−20.60	17.9772	.9963
.05	−20.40	−18.90	17.9763	.9940
.10	−19.15	−17.00	17.9736	,9902
.20	−17.35	−14.20	17.966	.9829
.35	−15.30	−11.15	17.951	.9726
.50	−13.65	−8.65	17.933	.9629
.75	−11.35	−5.25	17.895	.9478
1.00	−9.50	−2.30	17.848	.9338
1.25	−7.80	0.25	17.796	.9209
1.50	−6.28	2.60	17.738	.9088
2.00	−3.50	6.90	17.603	.8872
2.50	−1.03	10.65	17.451	8684
Sodium Bromide				
0.00	−24.50	−24.50	17.9776	0.9979
.01	−23.25	−22.60	17.9774	.9966
.02	−22.75	−21.80	17.9772	.9954
.05	−21.65	−20.10	17.9763	.9917
.10	−20.40	−18.20	17.9736	.9857
.20	−18.60	−15.45	17.966	.9741
.35	−16.55	−12.30	17.951	.9576
.50	−14.90	−9.75	17.931	.9420
.75	−12.55	−6.10	17.891	.9177
1.00	−10.50	−3.00	17.843	.8953
Sodium Iodide				
0.00	−24.80	−24.80	17.9776	0.9979
.01	−23.20	−22.45	17.9774	.9962
.02	−22.60	−21.55	17.9772	.9945
.05	−21.30	−19.55	17.9760	.9894
.10	−19.80	−17.35	17.9733	.9812
.20	−17.70	−14.10	17.965	.9654
.35	−15.40	−10.50	17.947	.9430
.50	−13.50	−7.60	17.924	.9220
.75	−10.85	−3.70	17.881	.8897
1.00	−8.65	−0.40	17.829	.8603
Sodium Nitrate				
0.00	−12.00	−12.00	17.9776	0.9979
.01	−10.30	−9.45	17.9774	.9970
.02	−9.60	−8.35	17.9772	.9960
.05	−8.10	−6.10	17.9758	.9933
.10	−6.45	−3.45	17.9722	.9888
.20	−3.95	0.50	17.962	.9804
.35	−1.00	5.15	17.939	.9687
.50	1.45	9.10	17.909	.9579
.75	4.95	14.65	17.847	.9416
1.00	8.00	19.40	17.770	.9271
Potassium Chloride				
0.00	−28.50	−28.50	17.9776	0.9979
.01	−27.50	−27.00	17.9774	.9969
.02	−27.10	−26.45	17.9772	.9959
.05	−26.25	−25.15	17.9767	.9929
.10	−25.35	−23.75	17.9747	.9880
.20	−24.00	−21.70	17.969	.9785
.35	−22.50	−19.40	17.958	.9649
.50	−21.30	−17.55	17.944	.9518
.75	−19.55	−14.90	17.915	.9312
1.00	−18.10	−12.65	17.879	.9118
1.25	−16.80	−10.55	17.837	.8936
1.50	−15.60	−8.70	17.791	.8765
2.00	−13.45	−5.35	17.668	.8441
2.50	−11.55	−2.45	17.568	.8168
Potassium Bromide				
0.00	−29.70	−29.70	17.9776	0.9979
.01	−28.70	−28.15	17.9774	.9964
.02	−28.30	−27.50	17.9772	.9950
.05	−27.40	−26.30	17.9767	.9906
.10	−26.45	−24.75	17.9745	.9835
.20	−25.00	−22.60	17.969	.9698
.35	−23.45	−20.20	17.957	.9501
.50	−22.20	−18.20	17.942	.9314
.75	−20.35	−15.35	17.910	.9021
1.00	−18.80	−12.90	17.871	.8750
Potassium Iodide				
0.00	−30.10	−30.10	17.9776	0.9979
.01	−29.00	−28.20	17.9774	.9960
.02	−28.50	−27.45	17.9772	.9940
.05	−27.50	−25.80	17.9760	.9883
.10	−26.40	−23.95	17.9733	.9790
.20	−24.60	−21.20	17.965	.9611
.35	−22.45	−18.00	17.950	.9357
.50	−20.70	−15.25	17.929	.9119
.75	−18.20	−11.50	17.887	.8753
1.00	−16.20	−8.35	17.836	.8419

TABLE VIX (*Concluded*)

m	Φ	$\bar{c}_{p_2}$	$\bar{c}_{p_1}$	Sp. ht.
	Potassium Nitrate			
0.00	−17.20	−17.20	17.9776	0.9979
.01	−15.60	−14.75	17.9774	.9967
.02	−14.95	−13.75	17.9772	.9956
.05	−13.55	−11.50	17.9758	.9922
.10	−11.95	−9.10	17.9724	.9867
.20	−9.55	−5.35	17.963	.9763
.35	−6.75	−0.90	17.941	.9615
.50	−4.45	2.60	17.914	.9478
.75	−1.25	7.60	17.858	.9267
1.00	1.55	12.05	17.788	.9077
	Sodium Sulfate			
0.00	−50.0	−50.0	17.9776	0.9979
.01	−44.7	−42.2	17.9770	.9960
.02	−42.6	−38.8	17.9763	.9942
.05	−37.8	−31.6	17.9720	.9890
.10	−32.3	−22.6	17.9601	.9807
.20	−23.7	−8.5	17.923	.9657
.35	−14.0	5.8	17.852	.9460
.50	−6.40	15.80	17.778	.9287
.75	3.20	29.00	17.629	.9040
1.00	11.05	39.00	17.474	.8835
1.25	17.60	47.60	17.302	.8661
1.50	23.00	55.00	17.113	.8510
	Potassium Sulfate			
0.00	−60.6	−60.6	17.9776	0.9979
.01	−56.7	−54.7	17.9772	.9956
.02	−55.1	−52.4	17.9767	.9933
.05	−51.7	−47.1	17.9734	.9867
.10	−47.9	−41.0	17.9652	.9761
.20	−42.1	−31.8	17.941	.9562
.35	−35.2	−21.4	17.890	.9289
.50	−29.90	−13.40	17.829	.9042
.65	−25.30	−6.40	17.756	.8816

Discussion

In Figs. 3 and 4 are shown plots of the experimentally determined values of the apparent molal heat capacity, 9, for the ten salts. Since Φ is equal to $\Delta C_p/m$, a given error (in cal.) in the measurement of ΔC_p will appear as a larger or smaller error in 9 (in. cal.) on the plot, depending upon whether m is less than or greater than unity. For very small values of m this error becomes large and for the smallest measured concentration, m = 0.043, the error in Φ is about 23 times that in the actual measurement of ΔC_p. Nevertheless, the extrapolation of the data to m = 0 is fairly certain, as is shown in an examination of the plots. The average error in any given measurement of ΔC_p for all the runs is found to be 0.10 cal. For sodium chloride the average error in a given determination of ΔC_p is 0.06 cal.

The data for sodium and potassium chlorides, sodium sulfate, potassium sulfate, nitrate, bromide and iodide were obtained in the order named. The value of Φ when m is zero is identical with $\bar{c}_{p_2}°$. We find

$$\bar{c}_{p_2}°(\mathrm{KCl}) - \bar{c}_{p_2}°(\mathrm{NaCl}) = \bar{c}_p°(\mathrm{K}^+) - \bar{c}_p°(\mathrm{Na}^+) = -5.2 \text{ cal.} \qquad (17)$$

and

$$\bar{c}_{p_2}°(\mathrm{K_2SO_4}) - \bar{c}_p°(\mathrm{Na_2SO_4}) = 2\bar{c}_p°(\mathrm{K}^+) - 2\bar{c}_p°(\mathrm{Na}^+) = -10.6 \text{ cal.} = 2 \times (-5.3 \text{ cal.}) \qquad (18)$$

Within the limits of error of the extrapolation to zero concentration, these two results are identical and show that the partial heat capacities of ions at infinite dilution are additive.

Given the difference in $\bar{c}_p°$ for Na^+ and K^+, then, if $\bar{c}_{p_2}°$ is found for potassium bromide, iodide and nitrate, $\bar{c}_{p_2}°$ for sodium bromide, iodide and nitrate is known. This relation was utilized in extrapolating the curves for these latter salts on which relatively few measurements were made.

In Fig. 4 is plotted $\bar{c}_{p_2}$ against $m^{1/2}$ for sodium and potassium sulfates, while Fig. 5 gives $\bar{c}_{p_2}$ against $m^{1/2}$ for sodium and potassium chlorides, bromides, iodides and nitrates. The limiting values of the partial molal heat capacity of the various salts are given in Table VIII.

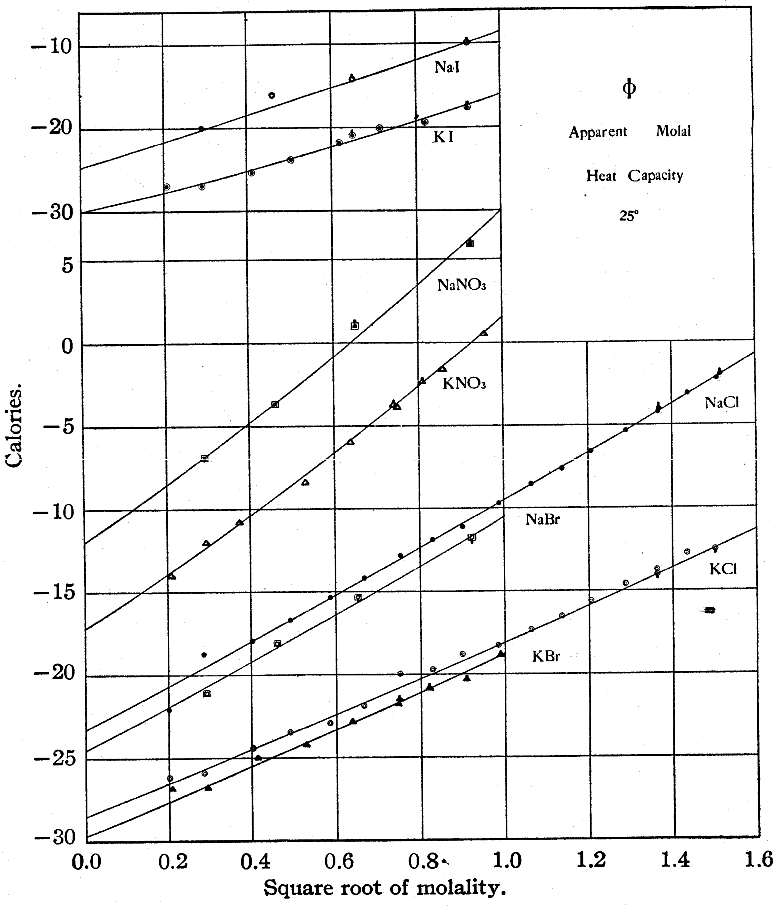


Fig. 3.

Table VIII

Summary of Values of $\bar{c}_{p_2}°$ (25°)

$NaNO_3$	−12.0 cal.	KNO_3	−17.2 cal.	$K^+ - Na^+$	− 5.2 cal.
NaCl	−23.3 cal.	KCl	−28.5 cal.	$SO_4^{--} - I^-$	− 0.2 cal.
NaBr	−24.5 cal.	KBr	−29.7 cal.	$I^- - Br^-$	− 0.3 cal.
NaI	−24.8 cal.	KI	−30.1 cal.	$Br^- - Cl^-$	− 1.2 cal.
Na_2SO_4	−50.0 cal.	K_2SO_4	−60.6 cal.	$Cl^- - NO_3^-$	−11.3 cal.

The values of the differences in the partial molal heat capacities of certain indicated ions at infinite dilution are given in the last column of Table VIII. They are found by subtracting the values for a pair of salts having a common ion.

$\bar{C}_{p_2}{}^\circ$ becomes increasingly negative for the positive ions in the order Na^+, K^+, and for the negative ions in the order NO_3^-, Cl^-, Br^-, I^-, SO_4^{--}. The value of $\bar{C}_{p_2}$ seems to increase to remarkably high values as the concentration is increased. For sodium sulfate at $m = 1.96$, $\bar{C}_{p_2}$ is 66.9 cal. This is more than twice the molal heat capacity of solid sodium sulfate, at the same temperature. At higher concentrations we should expect the value of $\bar{C}_{p_2}$ to become even larger.

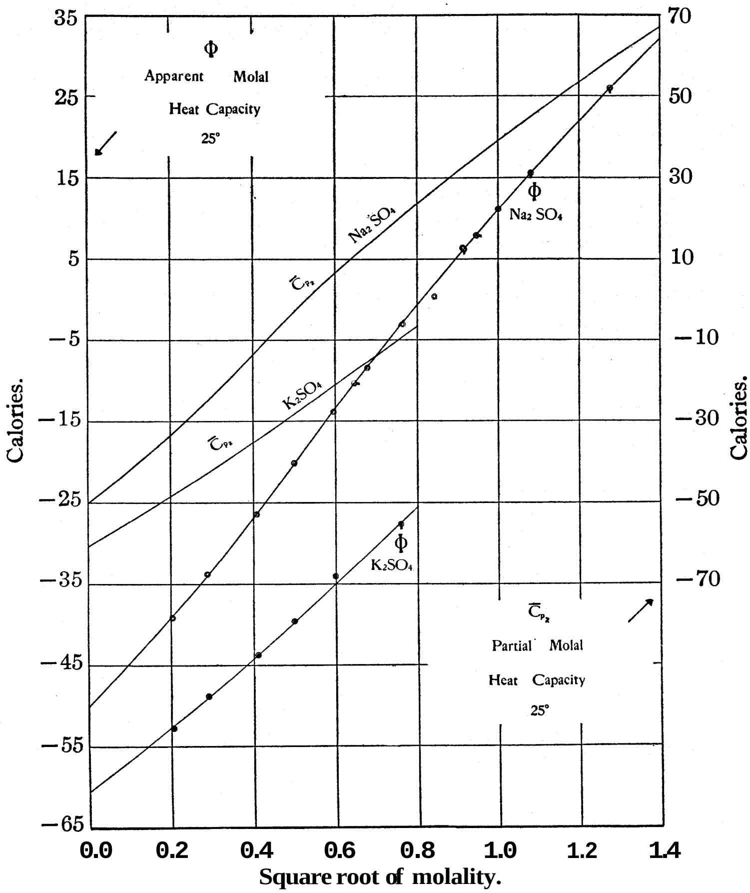


Fig. 4.

The Rate of Change of $\bar{C}_{p_2}$ with Molality

The introduction of a charged particle, as one sodium ion, into an atmosphere of electrical dipoles, as water molecules, changes the energy–temperature relations of all the water molecules within the sphere of influence of the ion in such a manner as to decrease the capacity of these water molecules to take up heat energy. The presence of the charged particle has restricted and damped the kinetic motion (and its temperature coefficient) of the dipoles. Then, too, there may be a direct attachment of a number of the dipoles to the charged body. These effects all make for a considerable decrease in the total number of degrees of freedom in the system, resulting in a diminution of the energy content and of the heat capacity. From these considerations it is easily seen why the apparent heat capacity of a strong electrolyte at infinite dilution is abnormally low, and in nearly every case negative.

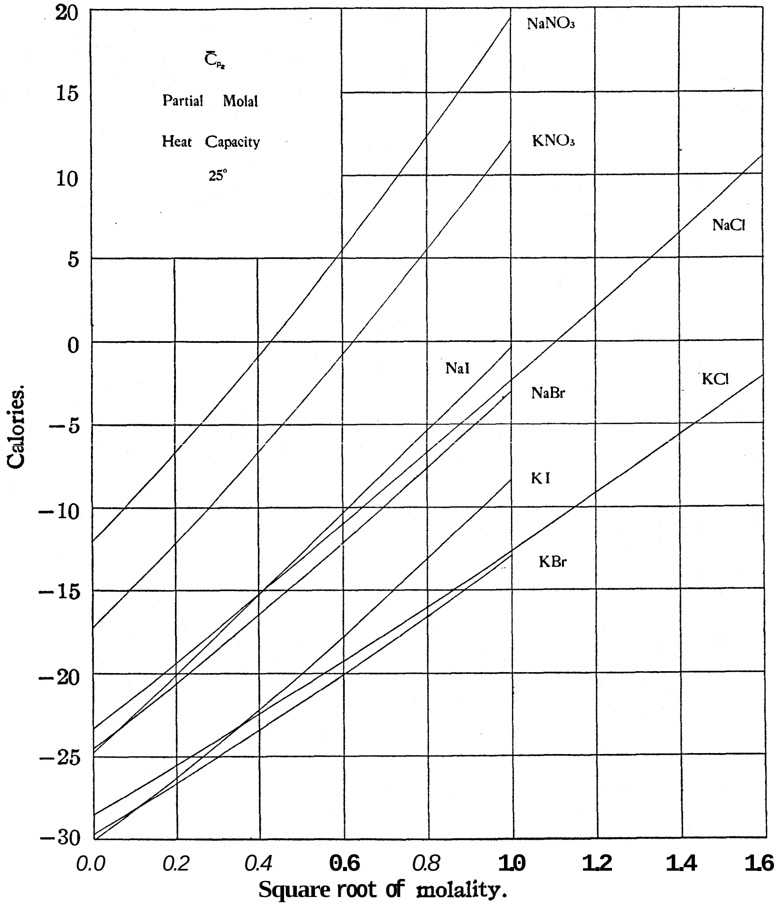


Fig. 5.

Zwicky[8] has attacked the problem of the heat capacity of electrolytic solutions by considering the electrolytic polarization of the water, the ionic atmosphere about a given ion, the compression of the solvent about the ion and the hydration of the ion. Bennewitz[9] considered the change in the intermolecular forces in seeking a theoretical solution of this problem.

Since at infinite dilution a given ion. can have within its sphere of influence only a definite number of water molecules, the effect which a given ion has upon the heat capacity of the water molecules will be independent of the source of the ion. The apparent heat capacity of a sodium ion, at infinite dilution, will be the same whether we obtain it from sodium chloride or from sodium sulfate. In other words, the apparent or partial molal heat capacities of ions at infinite dilution will be additive.[10] The effect that a given ion will have upon the capacity of the neighboring water molecules to absorb heat energy will depend upon the charge of the ion, the size of the ion and the configuration of the ion, if it is a polyatomic ion, such as nitrate or sulfate ion.

Randall and Ramage[4] found $\bar{C}_{p_2}$ to rise linearly with the square root of the molality. Their result is verified in the present measurements. We shall consider how the presence of other ions will affect the influence which a given ion has upon the water molecules. On the basis of the Debye-Hückel[11] theory of strong electrolytes one predicts that, in the dilute region, where the theory has been shown to be applicable, $\bar{C}_{p_2}$ should vary linearly with the square root of the concentration.[12]

Consider two systems, A consisting of an infinitely dilute solution, and B consisting of a solution of molality m. In going from State **A** to State B the change in the free energy of one mole of solute is $\bar{F}_2 - \bar{F}_2^\circ$. Following Debye and Hückel,[11a] we may separate this free energy change into two **parts,** the first of which is that due to the particles considered as solute molecules of **a** perfect solution, in which case the activity of the solute is equal to the concentration, and the second of which is the free energy change due to the fact that the particles are charged ions.

$$\Delta F = [\bar{F}_2\ (\text{class.}) - \bar{F}_2^\circ\ (\text{class.})] - [\bar{F}_2(\text{elec.}) - \bar{F}_2^\circ(\text{elec.})] \tag{19}$$

We can substitute for the second parenthesis the value given by Debye and Hiickel,

$$\bar{F}_2(\text{elec.}) - \bar{F}_2^\circ(\text{elec.}) = -\frac{Ne^2\Sigma\nu_i z_i}{2D}\,\frac{\xi}{1 + \xi\alpha} \tag{20}$$

---

[8] **Zwicky,** ***Physik. Z.,*** 27, 271 (1926).

[9] Bennewitz, Z. *Elektrochem.,* 33, 540 (1927).

[10] **A** statement which leads to this result **was** made by Lewis, THIS JOURNAL, 35, 15 (1913).

[11] (a) Debye and Hiickel, ***Physik.*** Z., 24, 185 (1923); (b) Debye, *ibid.,* 25, 97 (1924).

[12] Lange and Messner, *Z.* ***Elektrochem.,*** 33, 431 (1927), applied the Debye-Hückel theory in deriving the variation of $\bar{C}_{p_1}$ in the dilute region.

where $\xi^2 = 4\pi Ne^2\Sigma c_i z_i^2/1000\mathbf{D}kT$, and e is the electronic charge, D the dielectric constant of the medium, N Avogadro's number, k Boltzmann's constant, T absolute temperature, c concentration of solute in moles per liter, c_i concentration of i^{th} kind of ions in moles per liter, z_i charge on the $\mathbf{i}^{\text{th}}$ kind of ions, ν_i the number of the i^{th} kind of ions per molecule, and α a constant of the order or magnitude of the radius of the ion.

For $\bar{F}_2$ (class.) $-$ $\bar{F}_2°$ (class.) Debye and Hiickel write RT ln c, whence

$$\Delta F = -\frac{Ne^2\Sigma\nu_i z_i^2}{2\mathbf{D}}\,\frac{\xi}{1+\xi\alpha} + RT\ln c \tag{21}$$

But

$$T(\delta^2(\Delta F))/\delta T^2 = -\Delta C_p = -(\bar{c}_{p2} - \bar{c}_{p2}°) \tag{22}$$

Substituting Equation 21 in Equation 22, we find

$$\bar{c}_{p2} - \bar{c}_{p2}° = -T\frac{\delta^2}{\delta T^2}\left[-\frac{Ne^2\Sigma\nu_i z_i^2}{2\mathbf{D}}\,\frac{\xi}{1+\xi\alpha}\right] - T\frac{\delta^2\,(RT\ln c)}{\delta T^2} \tag{23}$$

Performing this differentiation and making the slight assumption that $\mathrm{d}c/\mathrm{d}T$ and $\mathrm{d}^2c/\mathrm{d}T^2$ are zero, we obtain

$$\bar{c}_{p2} - \bar{c}_{p2}° = \frac{3}{4}\left(\frac{\pi N}{1000k}\right)^{1/2}\frac{Ne^3}{(\mathbf{D}T)^{3/2}}f(\mathbf{D},\,T)(\Sigma\nu_i z_i^2)^{3/2}\frac{c^{1/2}}{(1+\xi\alpha)^2} \tag{24}$$

where

$$f(\mathbf{D},\,T) = 1 + 2\frac{T}{\mathbf{D}}\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}T} + 5\left(\frac{T}{\mathbf{D}}\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}T}\right)^2 - 2\frac{T^2}{\mathbf{D}}\frac{\mathrm{d}^2\mathbf{D}}{\mathrm{d}T^2} \tag{25}$$

In evaluating D, $\mathrm{d}\mathbf{D}/\mathrm{d}T$ and $\mathrm{d}^2\mathrm{D}/\mathrm{dT}^2$ we can take the values for pure water (which will not be very different from that of a very dilute solution) as taken from the equation of Adams[13] $\mathrm{D} = 400{,}000T^{-3/2}$ deduced from the measurements of Kockel.[14] For $\mathrm{T} = 298.1°K$, $\mathrm{D} = 77.75$; $\mathrm{d}\mathbf{D}/\mathrm{d}T = -0.3914$; $\mathrm{d}^2\mathrm{D}/\mathrm{dT}^2 = 0.003283$; $(T/\mathbf{D})(\mathrm{d}\mathbf{D}/\mathrm{d}T) = (\mathrm{d}\ln\mathbf{D})/(\mathrm{d}\ln\mathbf{T}) = -3/2$; $\mathrm{f}(\mathbf{D},\,\mathrm{T}) = 1.75$. Evaluating

$$\bar{c}_{p2} - \bar{c}_{p2}° = 2.14(\Sigma\nu_i z_i^2)^{3/2}[c^{1/2}/(1+\xi\alpha)^2] \tag{26}$$

In the dilute region $(1 + \xi\alpha)$ closely approaches the value of 1, and the concentration in moles per liter is very nearly the same as the concentration in moles per 1000 g. of water. Hence

$$\bar{c}_{p2} = 2.14(\Sigma\nu_i z_i^2)^{3/2}\,m^{1/2} + \bar{c}_{p2}° \tag{27}$$

The values of the valence factor $(\Sigma\nu_i z_i^2)^{3/2}$ (and 2.14 times the valence factor) for various types of solute are given in Table IX.

TABLE IX

SLOPE OF PARTIAL MOLAL HEAT CAPACITY AGAINST SQUARE ROOT OF MOLALITY

Valence type	1–1	2–1	2–2	3–1	3–2
$(\Sigma\nu_i z_i^2)^{3/2}$	2.82	14.7	22.6	41.6	165
$2.14(\Sigma\nu_i z_i^2)^{3/2}$	6.0	31	48	89	353

Equation 27 shows that in the dilute region in which the Debye-Hückel theory of strong electrolytes is applicable, $\bar{c}_{p_2}$, when plotted against the

---

[13] Adams, THIS JOURNAL, 48, 625 (1926).

[14] Kockel, *Ann. Physik*, [4] 77, 417 (1925).

square root of the concentration, should be a straight line whose slope will depend upon the charge and the number of the ions making up a solute molecule. This slope is the same for solutes of the same valence type and is greater for the higher valence types. It must be remembered that Equation 27 gives only the values of $\bar{c}_{p_2} - \bar{c}_{p_2}{}^\circ$. The value of $\bar{c}_{p_2}{}^\circ$ for any given pair of ions must be sought in some other manner.

The slopes of the curves of partial molal heat capacity against $m^{1/2}$ given in Figs. 4 and 5 at $m^{1/2} = 0$ are approximately as given in Table X.

TABLE X

APPROXIMATE LIMITING SLOPE OF PARTIAL MOLAL HEAT CAPACITY AGAINST SQUARE ROOT OF MOLALITY

Salt	NaCl	NaBr	NaI	Na_2SO_4	$NaNO_3$	KCl	KBr	KI	K_2SO_4	KNO_3
$\bar{c}_{p_2}/m^{1/2}$	19	18	23	76	25	15	15	18	62	25

In all the curves for the uni-univalent salts the slope is increasing somewhat with increase in $m^{1/2}$. For the sulfates there appears a point of inflection, at $m^{1/2} = 0.7$ for potassium sulfate and $m^{1/2} = 0.5$ for sodium sulfate.

According to Equation 27 and Table IX the value of the slope of $\bar{c}_{p_2}$ against $m^{1/2}$, in the dilute region, should be about 6 for a 1–1 and 31 for a 2–1 salt. The slopes given in Table X show an average of about 18 or 20 for the 1–1 and about 70 for the 2–1 salts. These values show the proper order of magnitude and about the right variation with change in the valence types of the salt. A closer agreement might possibly be obtained with a more precise knowledge of the true values of dD/dT and d^2D/dT^2, which are used in Equation 27, and by the non-neglect of the terms dc/dT and d^2c/dT^2. These results seem further to emphasize the validity of the assumptions underlying the Debye-Hückel theory of strong electrolytes as applied to dilute aqueous solutions.

The slopes of these curves of $\bar{c}_{p_2}$ increase in the order of Cl^-, Br^-, I^-, NO_3^- for the negative ions with a common cation and K^+, Na^+, for the positive ions with a common anion.

Other Ions

A complete review of all the available data on the specific heats of aqueous solutions of electrolytes was made to see if some values of $\bar{c}_{p_2}$ could be obtained on salts other than those measured in this work. In order that the data may be used to calculate Φ and by extrapolation to $m = 0$ find $\bar{c}_{p_2}$, the specific heat measurements must not only be reported to 1 in 10,000, but they must be precise to that extent. In comparatively few cases was the first requirement satisfied, and in these few there was lack of precision except in one or two cases. This, coupled with the fact that where the measurements were satisfying there were not enough of them in the dilute region to permit certain extrapolation to zero concentration, resulted in the securing of qualitative instead of quantitative information on values of $\bar{c}_{p_2}^\circ$ for additional salts.[15]

Using the data of Richards and Rowe,[15c,16] together with those here obtained, we find that the univalent positive ions can be arranged in the following order of decreasing (more negative) $\bar{c}_p^\circ$: Li^+, Na^+, K^+, H^+, Rb^+, Cs^+.

Combining the data of this work with those of Jauch[17] on potassium fluoride, we find the univalent negative ions in the following order of decreasing $\bar{c}_p^\circ$: F^-, Cl^-, Br^-, I^-.

The Jauch data also furnish the following qualitative information. In order of decreasing $\bar{c}_p^\circ$ we find Na^+, Mg^{++}, Al^{+++}. We also find $\bar{c}_p^\circ$ for Mg^{++} more negative than that for Be^{++}.

From the data of Cohen, *et al.*,[18] we find that $\bar{c}_p^\circ$ for Cd^{++} is more negative than for Zn^{++}.

The above information tells us that in any given group of the elements $\bar{c}_p^\circ$ becomes more negative as the atomic number increases and, in any given period, $\bar{c}_p^\circ$ becomes more negative as the charge on the ion increases.

The fact that H^+ does not fall into the regular order of the univalent positive ions indicates that it has some unique effect on the water molecules.

An ion at infinite dilution in water can be pictured as having oriented about it a number of water molecules (considered as electrical dipoles), some of which will be directly attached to the ion.[19] On this picture the partial molal heat capacity of the ion at infinite dilution will be the sum of three effects: $\bar{c}_p^\circ = A + B + C$, where A is the intrinsic heat capacity of the ion and has a positive value; B is the effect due to the breaking up of the ion hydrate (ion plus the directly attached water molecules) on the absorption of heat in the reaction: ion hydrate = ion + water molecules (for this reaction heat is absorbed and ΔH is positive; B has a positive value) and *C* is the effect that the charged body has on the heat capacity

---

[15] An example of the inadequacy of some of the specific heat data in giving proper values of $\bar{c}_{p_2}^\circ$ is the following: (a) Lewis and Randall (ref. 2, p. 86) give $\bar{c}_{p_2}^\circ$ for H_2SO_4 in aqueous solution as calculated from the specific heat data of (b) Biron, J. *Russ. Phys.-Chem. Soc.*, 31, 190 (1899), as 10.4 cal. From the specific heat data of (c) Richards and Rowe, THIS JOURNAL, 42, 1621 (1920), and of (d) Wrewsky and Kaigorodoff, Z. *physik. Chem.*, **112,** 83 (1924), and the heat of solution data at various temperatures of (e) Wrewsky and Sawaritzky, *ibid.*, 112, 92 (1924), one finds that $\bar{c}_{p_2}^\circ$ for HCl is about -34 cal. But $\bar{c}_{p_2}^\circ$ for NaCl is -23.3 cal. Hence $2\bar{c}_p^\circ(H^+) - 2\bar{c}_p^\circ(Na^+) = -21$ cal. Since $\bar{c}_{p_2}^\circ(Na_2SO_4)$ is -50 cal., $\bar{c}_{p_2}^\circ(H_2SO_4)$ should be about -71 cal.

[16] Richards and Rowe, THIS JOURNAL, 43, 770 (1921).

[17] Jauch, Z. *Physik,* 4, *441* (1920).

[18] (a) Cohen and Moesveld, Z. *physik. Chem., 95,* 305 *(1920);* (b) Cohen, Helderman and Moesveld, *ibid.,* 112, 135 (1924).

[19] Ghosh, *Trans. Faraday Soc.,* 15, 159 (1919).

of the water dipoles due to the restriction it places upon their motion, decreasing their capacity to absorb heating energy. (C has a negative value.)

Since $\bar{c}_p^{\circ}$ for all the ions here investigated is negative, A + B is less than C. Since $\bar{c}_p^{\circ}$ for K^+ is less than that for Na^+, and since A is very nearly the same for both Na^+ and K^+, then B + C is algebraically less (more negative) for K^+ than for Na^+. Since we should expect *C* to be more negative for the ion exerting the greatest electrical force upon the water molecules, then for ions of like charge *C* will be more negative for the smaller ion. Hence B must be greater for Na^+ than for K^+. This means that the temperature coefficient for the heat absorbed in the reaction

$$Na^+(H_2O)_{n_1} = Na^+ + n_1H_2O \tag{28}$$

is greater than that for the reaction

$$K^+(H_2O)_{n_2} = K^+ + n_2H_2O \tag{29}$$

This may be explained by assuming that n_1 is greater than n_2. This is in qualitative agreement with the data on the hydration of ions as given by various investigators.

Reverting to the unique effect observed in the case of H^+, we may postulate the formation of hydronium ion, H_3O^+, for which there is very good evidence from other sources. Effect *C* for H^+ will be large since it is reasonable to suppose that the intrinsic heat capacity of H_3O^+ is less than the sum of the intrinsic heat capacity of H_2O and that of H^+. This need not be a necessary argument in proving why $\bar{c}_p^{\circ}$ (H^+) is more negative than that for K^+ or Na^+, because Effect B will be less in the case of H_3O^+ since it will be larger and hence less hydrated than K^+ or Na^+.

Any consideration of the existence of $(H_2O)_2$ and $(H_2O)_3$ molecules as the molecular state of the water will not invalidate the foregoing arguments.

In the case of polyatomic ions, such as NO_3^- and SO_4^{--}, the configuration, as well as the charge and size, will play a predominant part in determining the value of $\bar{c}_p$".

Let us now consider the cause of the rapid increase in $\bar{c}_{p_2}$ with the concentration. This is obviously due to the fact that Effect C is becoming less negative as the concentration is increased because each ion is affecting fewer water molecules, or the effect per ion is less.

Another point to be considered is the almost linear relationship between $\bar{c}_{p_2}$ and $m^{1/2}$ throughout all the concentrations measured. For an electrolyte the logarithm of the activity coefficient can be approximately expressed in terms of the first two powers of $m^{1/2}$

$$\ln \gamma = Am^{1/2} + Bm \tag{30}$$

also

$$RT \ln \gamma = \bar{F}_2 - \bar{F}_2^{\circ} \tag{31}$$

Since $-(\bar{c}_{p_2} - c_{p_2}^{\circ})$ is $T\,\delta\,(\bar{F}_2 - \bar{F}_2^{\circ})/\delta T^2$ and if $\bar{c}_{p_2} - \bar{c}_{p_2}^{\circ}$ very nearly varies as $m^{1/2}$, this means that probably d^2B/dT^2 is zero. In other words, the physical properties which determine the value of B in the above equation have a temperature coefficient which is itself independent of the temperature.

For the data of Wrewsky and Kaigorodoff,[15d] who measured the specific heat of hydrochloric acid at various temperatures, and comparing Richards and Rowe's[16] 18° data with our 25° data we find that approximately $d\bar{c}_{p_2}°/dT$ is about 0.2 cal. per deg. around 25" for a uni-univalent electrolyte.

This agrees with the results of Randall and Ramage,[4] who found that in a dilute solution of sodium chloride, $\bar{c}_{p_2}$ increased with the temperature. This is in complete accord with the arguments presented here, since the polarizing and orienting effect of the ion upon the water molecules will decrease with increase in the kinetic energy of the dipoles.

From the values of $\bar{c}_{p_2}°$ obtained in this research, it can be stated definitely that for the reaction of dissolving one mole of a substance which is a strong electrolyte in a very large amount of water, AH will decrease with increase in temperature.

Given the reaction

$$MX(s) + n_1H_2O = M^+(m) + X^-(m) + n_1H_2O \qquad (32)$$

If n_1 is taken so large as to make the molality practically zero, we may write

$$MX(solid) = M^+(m = 0) + X^-(m = 0) \qquad (33)$$

Now we have shown that $\bar{c}_p°$ (M^+) + $\bar{c}_p°$ (X^-) is negative. Then $\Delta C_p = d\Delta H/dT$ is negative. Of course ΔC_p will be negative even though $\bar{c}_p°$ (M^+) + $\bar{c}_p°$ (X^-) be positive, provided the latter sum be less than the heat capacity of the solid.

In the case of a substance giving polyatomic ions, $\bar{c}_{p_2}°$ may be positive but will be less than the heat capacity of the pure substance. For very weak electrolytes, such as mercuric chloride and cadmium iodide, $\bar{c}_{p_2}°$ has a positive value which may be greater than the heat capacity of the solid.

In conclusion, we wish to express our thanks to Messrs. Jack Sherman, Albert Sherman and Bernard Weidenbaurn for their assistance in drawing Figs. 1 and 2, and in recalculating the specific heat data of other investigators; and to Mr. G. F. Nelson for building much of the apparatus.

Summary

The assembly of a calorimeter having a precision of greater than 0.1 per mille in measuring differentially the heat capacities of aqueous salt solutions is described, and a description of its calibration and method of operation for direct and for differential heat capacity measurements is given.

Methods of determining and calculating Φ, the apparent molal heat capacity of the solute, $\bar{C}_{p_2}$, the partial molal heat capacity of the solute, $\bar{C}_{p_1}$, the partial molal heat capacity of the solvent and the specific heat of the solution are given.

Tables and plots of the experimental data and tables of rounded values of Φ, $\bar{C}_{p_2}$, $\bar{C}_{p_1}$ and specific heat are given for the nitrates, chlorides, bromides, iodides and sulfates of sodium and potassium in aqueous solution from infinite dilution to 1.0 molal, and in some cases to 2.5 molal.

A theoretical equation for $\bar{C}_{p_2} - \bar{C}_{p_2}^{\circ}$ is derived on the basis of the Debye-Hückel theory of strong electrolytes in aqueous solution, and is compared with the experimentally determined values. ($\bar{C}_{p_2}^{\circ}$ refers to infinite dilution.)

The partial molal heat capacity of a given ion is shown to depend upon the charge, the size and the configuration of the ion. The partial molal heat capacities of ions are shown to be additive at infinite dilution.

The relation of the results obtained to hydration of ions and the temperature coefficient of the heat of solution of a strong electrolyte in a large amount of water is discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NO. 585]

THE REDUCTION OF PERMANGANATE ION BY CHROMIC ION IN ACID SOLUTION

BY H. A. FALES AND P. S. ROLLER[1]

RECEIVED AUGUST 8, 1928 PUBLISHED FEBRUARY 5, 1929

The peculiar nature of the reduction of permanganate ion in acid solution has long interested chemists. As early as 1866 Harcourt and Esson[2] in their study of the reduction of permanganate by oxalic acid observed that the reaction was autocatalytic and catalyzed by manganous ion, and that in the presence of the latter excess of oxalic acid slowed down the rate of oxidation. They imputed the catalytic effect to the formation of manganese dioxide in solution.

In 1903 the study of the reduction by oxalic acid was again undertaken by Schilow,[3] who endeavored to show that the autocatalysis was due to the interaction between the permanganate and a trivalent manganic oxalate complex, the primary reduction product.

The same reaction was next studied by Skrabal,[4] who observed a period

[1] This paper is constructed from a dissertation submitted by P. S. Roller in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[2] Harcourt and Esson, *Phil. Mag.*, 201 (1866).

[3] Schilow, *Ber.*, 36, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, 42, 1 (1905).

of comparatively rapid reduction which he called the induction period. In this period the interaction between the manganous ion which had been liberated in the so-called incubation period and the permanganate ion *induced* a rapid oxidation of the oxalic acid. In the presence of excess manganous ion, this author discovered the reaction to be unimolecular. This result was imputed to the unimolecular decomposition of the trivalent manganic ion complex already postulated by Schilow.

The work of Krutweig[5] shows that the reduction of permanganate by tartaric acid is exactly similar to that by oxalic acid; that the same holds true for lactic and citric acids is indicated by the recent work of Dey and Dhar.[6]

The tendency of trivalent manganic ion to enter into a complex compound with anions, particularly of organic acids, has been frequently affirmed. Salts of the manganic complex with malonic and oxalic acids have recently been prepared by Meyer and Schramm,[7] the compositions of the complex acids being $H_3[Mn(C_3H_2O_4)_3]$ and $H_3[Mn(C_2O_4)_3]$.

In order to obtain a clearer understanding of the mechanism of the reduction of permanganate ion, it seemed desirable to study the reduction in a medium free from the disturbing influence of complex compound formation between the trivalent manganic ion and the reductant. Chromic ion, which reduces permanganate ion in acid solution slowly at 25°, was chosen because as a metallic cation it met this requirement of non-complex formation.

Method of **Experiment and Analysis of Reaction Mixture.**—Experiments were conducted at 25.1°. After coming to temperature potassium chrome alum solution was rapidly pipetted into a prepared permanganate solution, which contained sulfuric acid and any other reagents whose effect was to be determined. (In the experiments with "MnO_2 dissolved in H_2SO_4," the MnO_2 in solution was formed by allowing $MnSO_4$ to interact with the prepared $KMnO_4$ solution for sixteen minutes before the addition of the chrome alum.)

The chrome alum and the sulfuric acid were in excess. The concentrations were: MnO_4^-, 0.00144 *M;* Cr^{+++}, 0.0227 *M;* H_2SO_4, 2.92 *M.* All other concentrations are expressed as a ratio of these.

At definite intervals of time, 25 cc. of the reaction mixture was rapidly pipetted into a solution consisting of 60 cc. of 1.2 M sulfuric acid and 25 cc. of 0.5 M potassium bromide. Free bromine was instantly liberated by the MnO_4^-, and was extracted by carbon disulfide purified according to the method of Allery.[8] The $Cr_2O_7^{--}$ which had been formed in the reaction was titrated electrometrically with 0.01 N ferrous sulfate.

---

[5] Krutweig, *Z. physik. Chem.*, 2,787 (1888).

[6] Dey and Dhar, Z. *Elektrochem.*, 32, 586 (1926).

[7] Meyer and Schramm, *Z. anorg. allgem. Chem.*, 123, 56 (1922); 157, 190 (1926).

[8] Allery, *Bull. soc. chim.*, [2] 35,491 (1881).

To avoid reduction of the $Cr_2O_7^{--}$ by Br^- or by carbon disulfide, all analytical operations had to be carried out in the absence of sunlight.

The platinum electrode was steamed between titrations and occasionally immersed in cold cleaning mixture. All vessels were steamed before use.

The electrometric titration had to be completed with little delay and one might not run past the end-point, as the back titration was inaccurate.

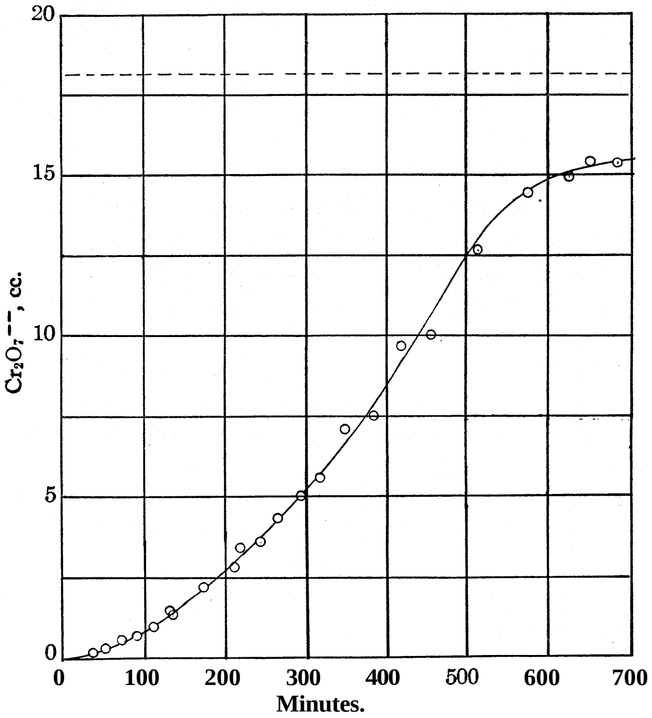


Fig. 1.—Reduction of MnO_4^- by Cr^{+++} in sulfuric acid solution at 25.1°.

The analysis of a series of prepared reaction mixtures showed the method to be accurate to ±0.05 cc. Check was frequently made on the analytical method.

It later occurred to the authors that it might be labor-saving to sweep out the dissolved bromine with air but this modification was not adopted in any of these experiments.

Reduction of MnO_4^- by Cr^{+++} in 2.92 M Sulfuric Acid Solution at 25.1°.—In Table I are given the results obtained in the direct reduction of MnO_4^- by Cr^{+++} ion. In the first column is the time in minutes from the instant that the chrome alum was added; in the second column is given the cc. of $Cr_2O_7^{--}$ (0.01 N) produced at the end of the corresponding time. The results of this table are plotted in Fig. 1.

Table I

Reduction of MnO_4^- by Cr^{+++} at 25.1°

Initial concentrations: MnO_4^-, 0.00144 *M*; Cr^{+++}, 0.0227 *M*; H_2SO_4, 2.92 *M*.

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
30.92	0.18	217.3	3.40	444.7	9.94
51.42	.30	241.1	3.65	513.2	12.70
71.42	.59	263.8	4.30	575.2	14.40
89.70	.72	293.2	4.97	625.5	14.78
110.1	.98	318.0	5.56	649.5	15.38
130.0	1.46	348.9	7.10	683.2	15.28
134.2	1.30	383.0	7.49	712.4	15.35
173.2	2.23	418.4	9.68	∞	18.20
209.9	2.78				

From the figure it is seen that the initial slow oxidation is rapidly autocatalyzed to an almost linear rate of oxidation. This rate finally falls off rather abruptly to a slow retarded rate of reaction at a point several cc. below the maximum degree of oxidation. There is a close resemblance between the results here obtained and those of Schilow[3] on the oxidation of oxalic acid.

From the change in the magnitude of the initial rate of oxidation with a change in the MnO_4^- and Cr^{+++} concentrations, the order of this reaction may be determined. A number of points were determined in the neighborhood of the origin, a smooth curve was drawn and the time required for a given degree of oxidation read off from the curve. The results for different initial MnO_4^- and Cr^{+++} ion concentrations are shown in Table II.

Table II

Order of the MnO_4^-–Cr^{+++} Reaction in Sulfuric Acid Solution

Relative MnO_4^- concentration	1	2	1
Relative Cr^{+++} concentration	1	1	0.5
$Cr_2O_7^{--}$, cc.	Minutes	Minutes	Minutes
0.1	23	11	40
.2	36	18	70
.4	58	32	113
.6	77	44	148

It is seen from Table II that doubling the MnO_4^- concentration doubles the initial rate of oxidation, while decreasing the Cr^{+++} concentration by one-half produces a corresponding decrease in the initial rate. The order of the reaction between MnO_4^- and Cr^{+++} with the latter in excess is therefore bimolecular and, since the oxidation of the Cr^{+++} is presumably to the hexavalent state, the reaction may be represented by the following equation, in which the reduction of MnO_4^- is to the tetravalent Mn.

$$MnO_4^- + Cr^{+++} = CrO_4^{--} + Mn^{++++} \qquad (1)$$

The effect on the reaction between MnO_4^- and Cr^{+++} of changing the concentration of the sulfuric acid was determined in the same way. The results are shown in Table III.

TABLE III

EFFECT OF SULFURIC ACID ON THE MnO_4^--Cr^{+++} REACTION

Relative sulfuric acid concentration	1	0.6
$Cr_2O_7^{--}$, cc.	Minutes	Minutes
0.1	23	21
.2	36	30
.4	58	44
.6	77	54

From Table III it is seen that reducing the sulfuric acid concentration by one-half produces little effect on the rate of oxidation initially. Neglecting the purely ionic effects of changing the sulfuric acid concentration, this result is in accordance with the reaction expressed by Equation 1, since the hydrogen-ion concentration does not enter. As the oxidation proceeds, the effect of decreasing the acidity becomes more and more marked, resulting in an increase in the rate of oxidation. This is due to the strong effect of acid on the autocatalysis.

Oxidation of Cr^{+++} by Manganese Dioxide Dissolved in Sulfuric Acid.—As already indicated, by manganese dioxide dissolved in sulfuric acid we mean the mixtures obtained on adding Mn^{++} to MnO_4^- in acid solution. In the course of the oxidation of Cr^{+++} by MnO_4^- the products of the interaction between MnO_4^- and Mn^{++} will be present in solution. Since the oxidation rate of these products exceeds that of the permanganate itself, it was important, in order to obtain an insight into the nature of the permanganate reduction by chromic ion, to study their oxidation properties. To do this we measured the oxidation rate of mixtures of MnO_4^- and Mn^{++}, obtained by adding the latter to the former contained in sulfuric acid solution, such as would virtually be present in the course of the reduction of the MnO_4^- ion.

TABLE IV

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 M H_2SO_4

Ratio $Mn^{++}/MnO_4^- = 0.42$

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.30	0.26	104.8	5.71	225.8	13.30
15.50	.85	129.5	7.40	246.7	14.18
30.43	1.59	154.8	8.75	288.1	14.69
55.17	2.96	180.8	10.85	310.8	14.82
81.18	4.86	205.5	12.50	346.7	15.02

TABLE V

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 M H_2SO_4

Ratio $Mn^{++}/MnO_4^- = 2.11$

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.05	1.27	55.45	9.70	253.5	13.98
11.35	2.54	82.64	10.93	357.7	14.33
19.95	4.66	111.3	11.89	447.0	14.71
35.00	7.23	142.0	12.12	617.5	15.08

TABLE VI

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 *M* H_2SO_4

Ratio $Mn^{++}/MnO_4^- = 4.22$

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.38	2.04	42.88	7.28	195.1	12.58
10.60	3.57	81.47	9.54	268.6	13.81
20.27	5.58	111.9	11.20		

The results which were obtained for different ratios of Mn^{++} to MnO_4^- are shown in Tables IV, V and VI, and are also plotted in Fig. 2 as Curves A, B and C, respectively.

In Curves A, B and C of Fig. 2, where the ratios of Mn^{++} to MnO_4^- are 0.42, 2.11 and 4.22, respectively, the initial rate of oxidation of the Cr^{+++} is seen to increase with increase in the ratio. On the contrary, the extent of oxidation after a sufficient period of time is greater in inverse order. This is seen to be due to the fact that the initial rate of oxidation falls off more rapidly the higher the ratio of Mn^{++} to MnO_4^-. Indeed, at a ratio 0.42 the curve is linear up to 14 cc. of $Cr_2O_7^{--}$, and at a ratio of 2.11 it is linear up to 6 cc. of $Cr_2O_7^{--}$.

An interpretation of these results throws considerable light on the question of the relationship of MnO_4^- to its ions of lower valence and their relative oxidizing characteristics.

Interaction between MnO_4^- and the Mn^{++} which has been added leads to the formation in acid solution of the trivalent Mn^{+++} ion and the tetravalent Mn^{++++} ion. Since these oxidize Cr^{+++} more rapidly than MnO_4^- itself, the reason for the increase in the initial rate of oxidation with increase in the ratio (up to 4.22) is understood.

The presence of excess MnO_4^- accounts for the initial linear rate of oxidation shown in Curves A and B. In the course of the oxidation the excess MnO_4^- interacts rapidly with the Mn^{++} which has been liberated to regenerate the reactive Mn^{+++} and Mn^{++++} and, indeed, since the rate is linear, in practically the same proportions in which they had originally been present.

The proportion of Mn^{+++} and Mn^{++++} may be estimated from the degree of linearity of the Curves A and B. Considering the latter, where the ratio of Mn^{++} to MnO_4^- is 2.11, the linearity extends over a period of 6 cc. of $Cr_2O_7^{--}$. Since this corresponds to the excess MnO_4^-, we find that the fraction of the total MnO_4^- which has been unacted on by the Mn^{++} added is, since 18.2 cc. of $Cr_2O_7^{--}$ corresponds to the complete reduction of the MnO_4^- to Mn^{++}, $^6/_{18.2}$, or close to $^1/_3$.

Let x be the number of moles of Mn^{+++} which has been formed, and a the initial total number of moles of MnO_4^-. The ratio of Mn^{++} to MnO_4^- being 2.11, and $^2/_3$ of the total MnO_4^- having interacted, the concentration of the Mn^{++++} which has been formed is $(2.78\,a - x)$. Since 5 Mn^{+++} is formed per mole of MnO_4^- and 5 Mn^{++++} for every 2 moles of MnO_4^- which have interacted, the follawing equation which accounts for the loss of MnO_4^- holds true

$$\frac{1}{5}x + \frac{2}{5}(2.78\,a - x) = 0.63\ a \tag{2}$$

Solving this equation for x, we obtain $x = 2.20$ a, $(2.78\,a - x) = 0.58$ a. Consequently, in this solution the Mn^{+++} is present to the extent of 79%, the Mn^{++++} to the extent of 21%.

Grube and Huberich[8] have measured the equilibrium between Mn^{++}, Mn^{+++} and Mn^{++++} in sulfuric acid solution. Mn^{+++} dissociates into Mn^{++++} and Mn^{++} according to the following equation

$$2\,Mn^{+++} = Mn^{++++} + Mn^{++} \tag{3}$$

The degree of dissociation is found to be augmented by a decrease in acidity due to the hydrolysis of the Mn^{++++} to MnO_3^{--}. Extrapolation from the results of these authors shows that at 2.92 M sulfuric acid the dissociation should be perhaps 80%. In the presence of MnO_4^- it should indeed be greater.

The preponderance of Mn^{+++} which we have shown to be present indicates that the interaction between MnO_4^- and Mn^{++} at a ratio of 2.11 leads to the initial formation of a large percentage of the trivalent Mn^{+++}, which having been formed dissociates but slowly into Mn^{++++}. This slow dissociation is probably due at least partly to the reversing action of the Mnf +++ present.

The Oxidation Properties of Mn^{+++} and Mn^{++++}.—To determine which of these ions oxidizes Cr^{+++} more rapidly, it is necessary to measure the initial rate after a known change in the proportion of the Mn^{+++} to Mn^{++++}. Now decreasing the acidity causes a shift to the formation of Mn^{++++}, manganese dioxide eventually being precipitated during the course of the oxidation if the acidity has been sufficiently decreased, say from 2.92 M sulfuric acid to 1.46 M sulfuric acid.

Under conditions corresponding to the results expressed in Table V and Curve B, Fig. 2, but with the acidity decreased by a fraction, the initial linear rate of oxidation was measured. The results are shown in Table VII, where the usual sulfuric acid concentration, 2.92 *M*, is expressed as unity.

TABLE VII

EFFECT OF CHANGING THE SULFURIC ACID CONCENTRATION ON THE OXIDATION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

Relative sulfuric acid concentration	1	0.8	0.65	0.5
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.332	0.348	0.396

---

[9] Grube and Huberich, *Z. Elektrochem.*, **29**, 8 (1923).

That the tetravalent Mn^{++++} oxidizes the Cr^{+++} more rapidly is seen from the fact that decreasing the sulfuric acid concentration results in an increase in the rate of oxidation.

The slow but continuous dissociation of Mn^{+++} into Mn^{++++} in its approach to the equilibrium concentration is demonstrated by increasing the period of incubation between the MnO_4^- and Mn^{++} previous to adding the Cr^{+++}. The results are shown in Table VIII, where it is seen that increasing the incubation period results in an increase in the rate of oxidation.

Table VIII

Effect of Changing the MnO_4^-–Mn^{++} Incubation Period

Incubation period, minutes	4	16	24	32
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.228	0.238	0.250	0.268

The tendency of Mn^{+++} to enter into complex ion formation with anions is well known. If it exists in complex formation with sulfuric acid, so that the dissociation of the Mn^{+++} into Mn^{++++} and Mn^{++} is preceded by its liberation from the complex, this should be reflected in a greater increase in the initial rate for a given increase in the incubation period when the sulfuric acid concentration is diminished.

Table IX

Effect of Changing the MnO_4^-–Mn^{++} Incubation Period—Sulfuric Acid Concentration Reduced by One-Half to 1.46 M

Incubation period, minutes	8	18
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.294	0.396

Comparing the results of Table IX with those of Table VIII, it is seen that at the lower acidity the effect of changing the incubation period is considerably more marked.

Müller and Koppe[10] and Holluta and Obrist[11] have shown that in the presence of fluoride ion the reaction between MnO_4^- and Mn^{++} goes completely to the formation of a trivalent manganic fluoride complex. In Table X are given the results obtained in the oxidation of Cr^{+++} by this complex formed by adding NaF to the MnO_4^- before the addition of excess Mn^{++}.

Table X

Effect of Fluoride Ion on the Oxidation of Cr^{+++} Ion by Manganese Dioxide Dissolved in Sulfuric Acid

$Mn^{++}/MnO_4^- = 4.22$. $F^-/Mn^{+++} = 4.04$

Minutes	10.62	20.62	40.73
$Cr_2O_7^{--}$ cc.	2.19	3.56	5.48

---

[10] Müller and Koppe, *Z. anorg. Chem.*, 68,160 (1910).

[11] Holluta and Obrist, *Monatsh.*, 41, 555 (1920).

Comparing the results of this table with those of Table VI, where the Mn^{++}/MnO_4^- ratio is also 4.22, it is seen that the rate of oxidation due to the fluoride ion complex is two-thirds that in the absence of fluoride ion. Such a small diminution in the rate leads again to the conclusion that in a 2.92 *M* sulfuric acid solution we have present primarily the $Mn^{+++}\cdot H_2SO_4$ complex rather than the free Mn^{+++}.

The Relative Proportion of Mn^{+++} and Mn^{++++} in Manganese Dioxide Dissolved in Sulfuric Acid.—In 2.92 M sulfuric acid, the addition of 2.11 moles of Mn^{++} per mole of MnO_4^- at 0.00144 M concentration leads as we have seen to the formation of 79% Mn^{+++} and 21% Mn^{++++}. How this proportion is affected by a change in the ratio can be determined by reference to Curve C, Pig. 2, where the ratio is only 0.42.

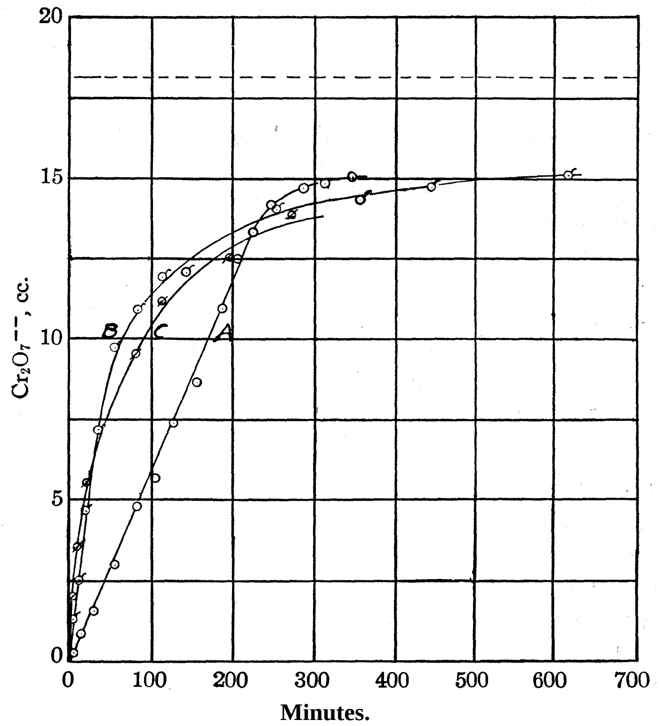


Fig. 2.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 25.1°. Curve A, Mn^{++}/MnO_4^- = 0.42; Curve B, Mn^{++}/MnO_4^- = 2.11; Curve C, Mn^{++}/MnO_4^- = 4.22.

Here the curve is linear up to 14 cc. of $Cr_2O_7^{--}$. By the same method of calculation previously employed, it is found that the percentages are here, 22% Mn^{+++}, 78% Mn^{++++}. Thus it is seen that with a decrease in the ratio of Mn^{++} to MnO_4^- there is a large increase in the proportion of Mn^{++++} to Mn^{+++}.

The Interaction between Mn^{++} and Mn^{++++}, and the Mechanism of the Oxidation by Mn^{+++}.—The magnitude of the interaction between Mn^{++} and Mn^{++++} to give Mn^{+++} may be inquired into by determining the effect of excess Mn^{++} on the rate of oxidation of Cr^{+++} by MnO_2 in sulfuric acid. For if Mn^{++} reduces the Mn^{++++} to the less reactive Mn^{+++} ion, its effect in excess would be to diminish the rate of oxidation of the Cr^{+++} to $Cr_2O_7^{--}$.

We will first set down the results obtained on the addition of Zn^{++} and Fe^{+++} ions. Zinc sulfate and ferric sulfate were added to the MnO_4^- in sulfuric acid previous to the addition of the Mn^{++}, the Cr^{+++} then being added in the usual way.

TABLE XI*a*

EFFECT OF Zn^{++} ON THE OXIDATION OR Cr^{+++} ION BY MANGANESE DIOXIDE DISSOLVED IN SULRURIC ACID

$Mn^{++}/MnO_4^- = 2.11$

Ratio of Zn^{++}/Mn^{++++}	0.0	0.063	0.31	0.92
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.315	0.285	0.290

TABLE XI*b*

EFFECT OF Fe^{+++} ON THE OXIDATION OR Cr^{+++} ION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

$Mn^{++}/MnO_4^- = 2.11$

Ratio of Fe^{+++}/Mn^{++++}	0.0	0.023	0.24
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.280	0.300

In Tables XI*a* and XI*b* the concentrations of the Zn^{++} and Fe^{+++} are expressed as their ratio in moles to the Mn^{++++} that would be present if the latter alone were formed by interaction between MnO_4^- and Mn^{++}. It is seen that a slight addition of Zn^{++} or Fe^{+++} cation produces an increase in the linear rate of oxidation. Further addition of these cations produces but little increase in the rate.

Having thus determined what the effect of Mn^{++} should be in its capacity as a cation, we set down in Tables XIIa and XIIb the results which

TABLE XIIa

EFFECT OB EXCESS Mn^{++} ON THE OXIDATION OF Cr^{+++} ION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

MnO_4^- concentration, 0.000576 *M*

Ratio of Mn^{++}/MnO_4^-	2.1111	7.38/1	15.8/1
Cc. of $Cr_2O_7^{--}$ after ten minutes	0.626	0.473	0.306

TABLE XIIb

EFFECT OF EXCESS Mn^{++} ON THE OXIDATION OR Cr^{+++} ION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

MnO_4^- concentration, 0.000288 M

Ratio of Mn^{++}/MnO_4^-	2.11/1	10.5/1
Cc. of $Cr_2O_7^{--}$ after ten minutes	0.225	0.108

were obtained with Mn^{++} in excess. The degree of oxidation after ten minutes is recorded against the ratio of Mn^{++} to MnO_4^-.

The effect of Mn^{++} in ratio greater than 4, contrary to the effect of the Zn^{++} and Fe^{+++} cations, is a progressive decrease in the oxidation rate as the ratio is increased.

We have already seen that the apparent oxidation rate of Mn^{++++} is greater than that of Mn^{+++}. The above results with Mn^{++} ion in excess can be explained then on the basis of a greater interaction between Mn^{++++} and the excess Mn^{++} to give the Mn^{+++} ion, as expressed in Equation 3.

Whence does the Mn^{++++} ion arise? This question is pertinent since we have seen that the greater the initial ratio of Mn^{++} to MnO_4^- the greater the proportion of Mn^{+++} which is formed. At a ratio exceeding 4, we should expect the formation solely of Mn^{+++}.

On this basis, the Mn^{++++} which interacts with the excess Mn^{++} comes from the subsequent dissociation of the Mn^{+++} initially formed. It thus appears that the oxidation of Cr^{+++} by Mn^{+++} is at least in part indirect, taking place in virtue of its dissociation into the reactive Mn^{++++}. The apparent oxidation rate of the Mn^{+++} decreases in the presence of excess Mn^{++} due to the greater reversal of this dissociation.

The potential of Mn^{+++} against Mn^{++} in 4.55 M sulfuric acid, decreasing with the acidity, is given by Grube and Huberich[8] as 1.503 v. Landolt-Bornstein "Tabellen," 1923, cite the normal electrode potential of $HCrO_4^-$ against Cr^{+++} as 1.3 v. The closeness of these values makes it appear likely that the oxidation of Cr^{+++} by Mn^{+++} is entirely indirect. Assuming this to be the case, the mechanism of the oxidation by the trivalent manganese is as follows.

$$\text{I} \quad Mn(HSO_4)_3 \text{ [complex]} \rightleftarrows Mn^{+++} + 3HSO_4^-$$

$$\text{IIa} \quad Mn^{+++} + Mn(HSO_4)_3 = Mn^{++++} + Mn^{++} + 3(HSO_4)^-$$

$$\text{IIb} \quad 2\,Mn^{+++} = Mn^{++++} + Mn^{++}$$

$$\text{III} \quad Mn^{++++} + Mn^{+++} + Cr^{+++} + 4H_2O = CrO_4^{--} + 2Mn^{++} + 8H^+$$

In Stage I we have the disengagement of the Mn^{+++} from its complex with the sulfuric acid. In Stages IIa and IIb the Mn^{+++} dissociates to form Mn^{++++}. In the third stage the Mn^{++++} oxidizes the Cr^{+++}, in conjunction with Mn^{+++}.

Skrabal[4] assumed that the rate of oxidation of oxalic acid in the presence of excess Mn^{++} was determined by the rate of dissociation of the Mn^{+++} ion from its oxalic acid complex. This rate of dissociation he found to be unimolecular. Dey and Dhar[6] found the oxidation of lactic and citric acids by the trivalent manganese also to be unimolecular.

If in accordance with these results we assume the rate of oxidation of Cr^{+++} in excess to be determined by the rate of the unimolecular disengagement of Mn^{+++} from its sulfuric acid complex we have

$$\frac{dx}{dt} = k_1 (a - x) \tag{4}$$

x is here the equivalent concentration of $Cr_2O_7^{--}$, a is the initial equivalent (or molar) concentration of Mn^{+++}, while $(a - x)$ is the molar concentration of the trivalent manganese at any instant.

Now the above equation is strictly true only when the tetravalent manganese, whose concentration is negligible against the trivalent manganese, is used up solely in its reduction by the Cr^{+++}. However, a fraction of it is reduced to Mn^{+++} by the excess manganous ion according to **(3)** as we have shown.

Let b represent the initial molar excess of Mn^{++}, so that $b + x$ is the concentration of Mn^{++} at any instant.

The rate of reduction of Mn^{++++} by Mn^{++} is given by the equation

$$R_1 = k_3\, Mn^{++++} (b + x) \tag{5}$$

The rate of reduction of Mn^{++++} by the Cr^{+++} in excess is, according to Stage III above, given by

$$R_2 = k_2\, Mn^{++++} (a - x) \tag{6}$$

From (5) and *(6)* the fraction of the Mn^{++++}, formed by the dissociation of the Mn^{+++}, which is reduced by the Cr^{+++} as against reduction by the Mn^{++} is

$$F = \frac{kt\,(a - x)}{(k_3b + k_2a) + (k_3 - k_2)x} \tag{7}$$

To take this reducing action of Mn^{++} into account a correction must be made to Equation 4 such that it is multiplied by the fraction F. We thus obtain finally for the rate of formation of $Cr_2O_7^{--}$

$$\frac{dx}{dt} = \frac{k_a\,(a - x)^2}{(k_b + x)} \tag{8}$$

where

$$k_a = \frac{k_1k_2}{k_3 - k_2} \tag{9}$$

$$k_b = \frac{k_3b + k_2a}{k_3 - k_2} \tag{10}$$

This equation may be integrated and reduced to the form given by (11), where K_2 and K_1 represent a bi- and unimolecular velocity constant, respectively

$$(k_b + a)K_2 - Kt = k_a \tag{11}$$

If we plot K_1 against K_2 we should by Equation *11* obtain a straight line whose slope is $(k_b + a)$ and whose intercept is k,. From the smoothed data of Table VI, K_2 and K_1 were calculated and plotted against each other as shown in Fig. **3.** **A** straight line is obtained with a slope of **23.0** and intercept *—0.0088.* With a = 18.2 cc., this gives $k_a = 0.0088$ and $k_b = 4.8$. Solving for k_3/k_2 and for k_1 by Equations 9 and *10,* with $b = 0.73$, we obtain $k_3/k_2 = 5.61$ and $k_1 = 0.0406$. The specific rate of reduction of Mn^{++++} by Mn^{++} is thus 5.61 times as great as that by Cr^{+++} in excess, while the constant for the unimolecular decomposition at 25° of the complex, $Mn(HSO_4)_3$, is 0.0406.

At 35.0' the results obtained in the oxidation of Cr^{+++} by Mn^{+++} are shown in Table XIII.

TABLE XIII

OXIDATION OR Cr^{+++} BY MANGANESE DIOXIDE IN SULFURIC ACID AT 35.0°

Ratio of Mn^{++}/MnO_4^- = 4.22. MnO_4^- = 0.001440 M

Minutes	4.00	9.55	19.90	35.00	56.95	89.42	149.3
$Cr_2O_7^{--}$, cc.	4.90	7.62	10.11	12.11	13.69	14.78	15.70

Calculation from the straight line obtained in plotting K_1 against K_2 (Fig. 4) shows that at 35.0' k_3/k_2 = 4.37, k_1 = 0.163. The temperature coefficient of the unimolecular decomposition of the complex $Mn(HSO_4)_3$ is therefore 4.01.

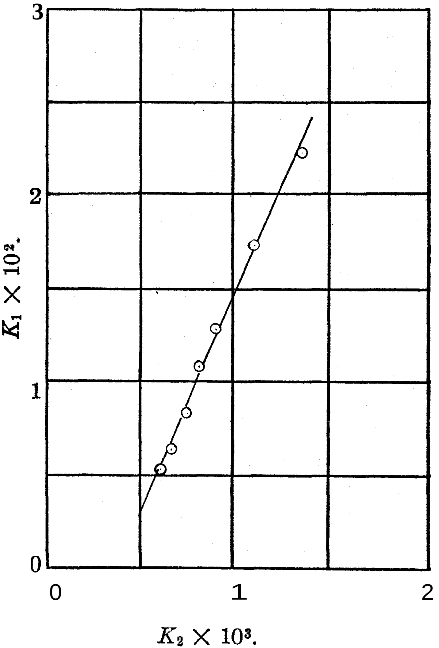


Fig. 3.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 25.1°. Mn^{++}/MnO_4^- = 4.22.

Order of the Oxidation by Manganese Dioxide Dissolved in Sulfuric Acid.—In the oxidation by manganese dioxide in sulfuric acid solution the order of the reaction with respect to Cr^{+++} is unity as is seen from the data of Table XIV.

The initial linear rate of oxidation is here 0.011 cc./min. as against 0.024 cc./min. when the Cr^{+++} concentration is twice as great (Table V).

In the presence of a mixture of tri- and tetravalent manganese we should expect in accordance with Stage III of the above reaction a bimolecular oxidation of the Cr^{+++} (in excess). Keeping the ratio constant at 2.11, where, at MnO_4^- = 0.00144 *M*, we have 79% of Mn^{+++}, 21% of Mn^{++++}, the initial linear rate of oxidation was measured with varying MnO_4^- concentration. The results are shown in Table XV.

TABLE XIV

OXIDATION OR Cr^{+++} BY MANGANESE DIOXIDE IN SULFURIC ACID AT 25.1°

Cr^{+++} concentration reduced by $^1/_2$. Ratio of Mn^{++}/MnO_4^- = 2.11

Minutes	6.25	18.12	38.08	69.62	140.2	221.9	328.8	442.4
$Cr_2O_7^{--}$, cc.	0.60	1.84	4.74	7.94	10.48	11.97	13.10	13.80

TABLE XV

INITIAL LINEAR RATE OF OXIDATION WITH CHANGE IN THE MANGANESE DIOXIDE CONCENTRATION

Relative manganese dioxide concentration	2.0	1.0	0.4	0.2[a]
$Cr_2O_7^{--}$, cc./min.	0.665	0.238	0.060	0.021

[a] The Mn^{++} remained in contact with the MnO_4^- for forty-five instead of the usual sixteen minutes.

If we plot the log of the rate of oxidation against the relative concentration, we obtain very closely a straight line whose slope is 1.5. This is therefore the apparent order of the oxidation of Cr^{+++} in excess by a mixture of the tri- and tetravalent manganese.

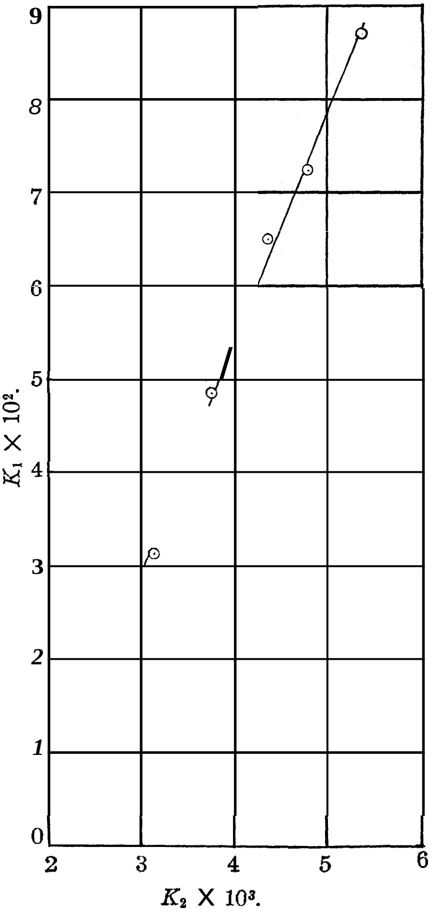


Fig. 4.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 35.0°. $Mn^{++}/MnO_4^- = 4.22$.

Now we have already observed that decreasing the concentration of Mn^{++} relative to MnO_4^- results in a shift in the proportion of Mn^{++++} to Mn^{+++} in favor of the tetravalent ion. The apparent fractional order of reaction found above can be explained on the basis of a similar shift with a decrease in the initial Mn^{++} concentration, though here the MnO_4^- concentration also changes.

Properties of the Reduction of MnO_4^- in Acid Solution.—We have shown that the oxidation by MnO_4^- in acid solution is accompanied by the oxidation due to the direct action of the tetravalent and the indirect action of the trivalent manganese. MnO_4^- itself oxidizes Cr^{+++} very slowly at 25°; Mn^{++++} oxidizes it rapidly. The action of Mn^{+++} takes place in virtue of its unimolecular disengagement from a complex compound with sulfuric acid with subsequent dissociation into Mn^{++++}. The latter is responsible for the oxidation of the Cr^{+++}. Mn^{++} reduces Mn^{++++} to the trivalent state. Thus the oxidation of Cr^{+++} by Mn^{+++} is retarded in proportion to the excess Mn^{++} present.

Since, ultimately, only Mn^{+++} in its usual complex form and an increasing excess of Mn^{++} are present, the marked end retardation observed in the oxidation of Cr^{+++} by MnO_4^- is explained.

We have shown that the interaction between Mn^{++} and MnO_4^- in 2.92 *M* sulfuric acid leads initially to the formation of Mn^{+++} and Mn^{++++}. The proportion of the latter is increased at a fixed MnO_4^- concentration by decreasing the Mn^{++} concentration.

On this basis, in the course of the oxidation of Cr^{+++} by MnO_4^-, the Mn^{++} which is first liberated forms the reactive Mn^{++++}. As the concentration of Mn^{++} tends to build up relative to the MnO_4^-, more and more of the trivalent manganese is formed, thus slowing up the autocatalysis until finally, since it alone is present, its own slow oxidation rate is measured.

The results obtained here in the reduction of MnO_4^- by Cr^{+++} show in several respects a striking similarity to the reduction by oxalic, tartaric and citric acids, etc. The chief difference lies in the fact that here the Mn^{+++} forms a complex with sulfuric acid, while there it forms a complex which is probably more stable with the reducing agent itself. By assuming as above an indirect oxidation by the Mn^{+++} complex and a very rapid oxidation by the Mn^{++++}, the properties of the permanganate reduction by these organic acids may be readily explained. In particular the so-called induction observed by Skrabal[4] in the oxidation of oxalic acid can be accounted for by the formation in the presence of slight amounts of Mn^{++} of the highly reactive Mn^{++++} by interaction between MnO_4^- and Mn^{++}.

Summary

The reduction of MnO_4^- by Cr^{+++} at 25.1° in sulfuric acid solution is autocatalytic and resembles closely the reduction by numerous organic acids, such as oxalic acid.

A study of the mechanism of the reaction reveals the presence of Mn^{++++} and of Mn^{+++} which is contained in a sulfuric acid complex. Oxidation by the latter is indirect in virtue of its unimolecular disengagement from the complex and its subsequent decomposition into Mn^{++++}, which oxidizes Cr^{+++} rapidly. The temperature coefficient between 25 and 35° of the unimolecular reaction is 4.01. Mn^{++++} also reacts with Mn^{++}, thus reverting to the non-reactive Mn^{+++}.

In the interaction between Mn^{++} and MnO_4^- in acid solution, the relative proportion of Mn^{++++} to Mn^{+++} increases with decrease in the ratio of Mn^{++} to MnO_4^-.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF MICHIGAN]

THE SOLUBILITY OF CALCIUM SULFATE FROM 0 TO 200°

BY EVERETT P. PARTRIDGE[1] AND ALFRED H. WHITE[2]

RECEIVED AUGUST 11, 1928 PUBLISHED FEBRUARY 5, 1929

The Literature on the Solubility of Calcium Sulfate

A search of the literature, complete up to May, 1928, covering references to the solubility of any of the various forms of calcium sulfate, was made and the original data abstracted from these articles were compared. Such as seemed significant have been utilized in conjunction with the determinations described in the present paper.

For the purposes of this paper all concentrations have been expressed in parts of $CaSO_4$ per million parts of solution. Conversion from original data has been carried out with the use of the density measurements of Hulett and Allen[3] on calcium sulfate solutions, although in view of the low solubilities encountered this is a refinement well within the experimental error.

The Solubility of Gypsum.—The lower curve of Fig. 1 represents the solubility of gypsum as determined by the values of Raupenstrauch,[4] Hulett and Allen,[3] Melcher,[5] and Cavazzi.[6] The excellent agreement of the four sets of data is checked by individual determinations at various temperatures made by other recent investigators.

It should be noted here that Raupenstrauch has never received the credit due him for the first accurate determination of the gypsum solubility curve. His article antedates the well-known and equally excellent work of Hulett and Allen by seventeen years but it has been quite generally ignored.

The Solubility of Calcium Sulfate Hemihydrate.—Marignac,[7] Potilitzin[8] and Cavazzi[6] found the solubility of dehydrated gypsum at room temperature to be approximately five times that of fully hydrated gypsum. That these values represent the solubility of calcium sulfate hemihydrate

---

[1] This paper forms part of the dissertation submitted by Dr. Partridge in partial fulfilment of the requirements for the Ph.D. degree at the University of Michigan. Acknowledgment is made to The Detroit Edison Company which sustained this work through a fellowship.

[2] Professor of Chemical Engineering, University of Michigan.

[3] G. A. Hulett and L. E. Allen, THIS JOURNAL, 24, 667–669 (1902).

[4] G. A. Raupenstrauch, *Monatsh.*, 6, 563–569 (1885).

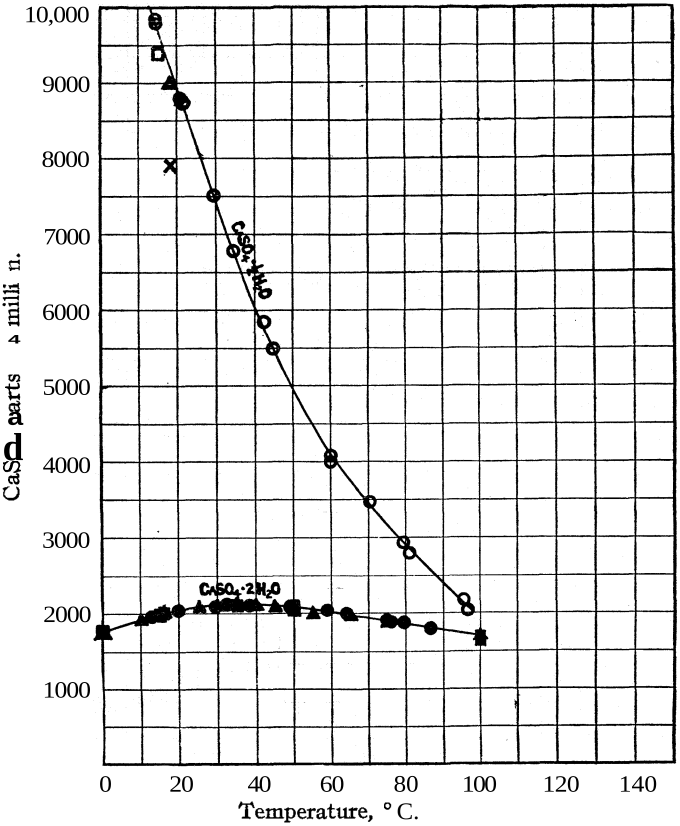
[5] A. C. Melcher, THIS JOURNAL, 32, 50–66 (1908).

[6] A. Cavazzi, *L'Industria Chimica*, 6, 366–368 (1904); *Chem. Centr.*, [5] 9, 1693–1694 (1905).

[7] C. Marignac, *Ann. chim. phys.*, [5] 1, 274–282 (1874).

[8] A. Potilitzin, *J. Russ. Phys.-Chem. Soc.*, 26, 170, 221–229 (1894); *Ber.*, 27, 613–616 (1894); *Chem. Centr.*, 515 (1894).

seems apparent from the values published by Chassevent,[9] in 1926, **for** this substance. The upper curve of Fig. 1 represents the solubility of the hemihydrate as determined by the data of the latter investigator, and shows the individual points previously reported. Chassevent found that hemihydrate solutions were very unstable at lower temperatures-but were relatively stable for a short range below 100°.



●, Raupenstrauch; ▲, Hulett and Allen; ■, Melcher; ⊡, Cavazzi; ×, Potilitzin; △, Marignac; ○, Chassevent.

Fig. 1.—Solubility of gypsum and hemihydrate at temperatures from 0–100° C. expressed in parts per million of CaSO$_4$.

The Solubility of "Soluble **Anhydrite.**"—It seems probable, at the present time, as a result of a series of investigations culminating in the work of Linck and Jung[10] and of Jung alone,[11] that only three crystal forms of

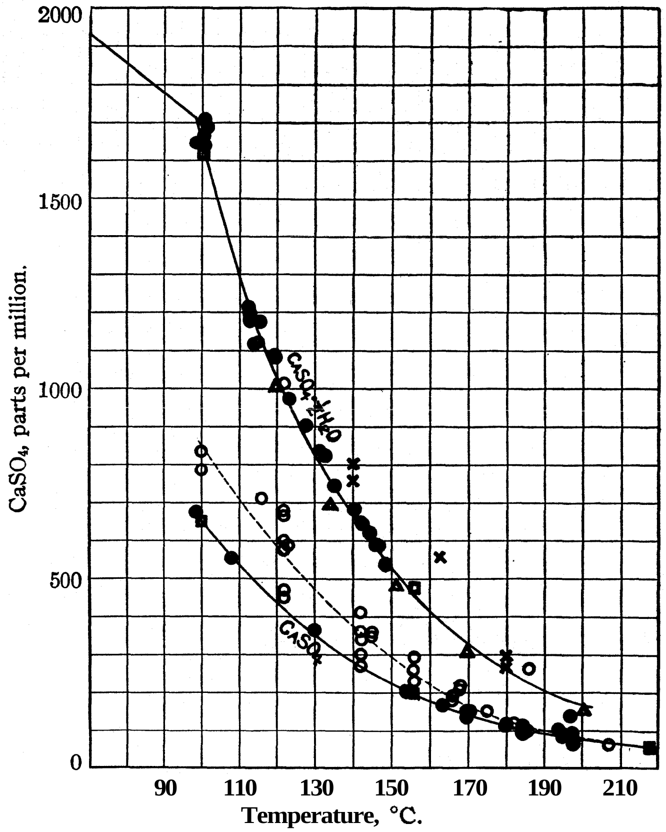
---

[9] L. Chassevent, Bull. *soc. encour. ind. nat.*, 789–803 (1926); *Ann. chim.*, [10] 6, 313–351 (1926).

[10] G. Linck and H. Jung, Z. *anorg.* Chem., 137,407417 (1924).

[11] H. Jung, *ibid.*, 142, 73–79 (1925).

calcium sulfate exist and that "soluble anhydrite," long a mystery, possesses the crystal structure of calcium sulfate hemihydrate. Evidence confirming this statement will be presented in the near future by Ramsdell and Partridge in a crystallographic study of the forms of calcium sulfate produced at various temperatures between 100 and 200° in contact, respectively, with water and with dry air. Additional circumstantial evidence will be shown in the present article from the fact that the solubility curve for hemihydrate below 100° found by Chassevent is continuous with the solubility curve above 100" previously ascribed to "soluble anhydrite."



×, Tilden and Shenstone; △, Boyer-Guillon; □, Melcher;
○, Hall, Robb and Coleman; ●, White and Partridge.

Fig. 2.—Solubility of gypsum, hemihydrate and anhydrite from 100 to 220° C. expressed in parts per million of $CaSO_4$.

When gypsum is the initial solid phase in contact with water, the solubility at temperatures above 100" is shown by the upper curve of Fig. 2, which is determined by the data of Boyer-Guillon,[12] Melcher[5] and Hall, Robb and Coleman[13] on "soluble anhydrite," and of the authors of this paper on calcium sulfate hemihydrate. The less accurate values of Tilden and Shenstone[14] are also shown.

This solubility curve for hemihydrate intersects that for gypsum at a temperature of approximately 98°, which is in excellent accord with the observation made by Davis,[15] and checked by the authors of this paper, that gypsum crystals in contact with water at 100° are gradually converted to hemihydrate.

The **Solubility of Anhydrite.**—Melcher[5] calculated the solubility of anhydrite at **100, 156** and 218° from conductivity measurements carried out with solutions of calcium sulfate in a platinum-lined bomb, using as solid phase either an initial addition of anhydrite or anhydrite formed from an initial addition of gypsum by maintaining the bomb at 218° for several hours. Hall, Robb and Coleman[13] made a series of direct determinations in a small laboratory boiler, using solutions of calcium sulfate in contact with a solid phase of anhydrite prepared by burning gypsum at a dull red heat in a muffle furnace for several hours. The dotted line of Fig. **2** is determined by the average values of the individual determinations of the latter investigators, while the bottom curve, determined by the authors of this paper, passes through the points found by Melcher.

Experimental Work

General Method.—Solubility values at intervals in the temperature range 100–200° were obtained by analysis of the sulfate content of samples removed from an experimental boiler housed in a thermostat which could be maintained for any desired period of time at a temperature constant to within **0.5".** This boiler was initially charged for each series of determinations with **10** liters of **a** solution of calcium sulfate saturated with gypsum at room temperature, to which solution was added **10** g. of precipitated gypsum powder. Solution samples were removed through a filter within the boiler and were cooled to **14–16'** in a cooling coil while still subjected to boiler pressure. The sulfate concentration of these samples was found gravimetrically by precipitation as barium sulfate.

Apparatus.—A photograph of the experimental boiler unit used in the authors' work is shown in Fig. 3. **This was used for the solubility work here described and also for a series of scale formation tests which will be described in the future. For the determinations of solubility the unit consisted essentially of the *boiler* proper, suspended within an *air thermostat,* fed by *a* small pump, and equipped with an *internal filter* connected to a *cooling coil* outside of the thermostat.**

---

[12] **A. Boyer-Guillon,** *Ann. conserv. arts metiers, [3]2,* 187–211 (1900).

[13] R. **E. Hall, J. A. Robb and *G.* E. Coleman,** THIS JOURNAL, 48,927–938 (1926).

[14] **W. A. Tilden and W. A. Shenstone,** ***Phil. Trans. Royal Soc. London, I,*** **175,** 23-36 (1884).

[15] **Davis,** ***J. Soc. Chem. Ind.,*** 26,727–738 (1907).

The *boiler* was a two-foot length of six-inch steam pipe. fitted with companion flanges. The boiler feed line and an exhaust line were tapped into the top flange, while the bottom flange carried a special plug which served to introduce the internal filter and to make connection between this filter and the external cooling coil.

The *air thermostat* was made of sheet steel with two spaced linings of transite to cut down heat radiation. It was heated by Chromel A resistance coils and rapid circulation of the air was maintained by a motor-driven fan. The temperature of the thermostat was controlled by a mercury column, the expansion of which operated a relay controlling the current through the heating coils. The fluctuation of the thermostat air temperature was rapid and was less than 0.5°. Such a fluctuation was considered negligible in view of the relatively great heat capacity of the boiler and its contents.

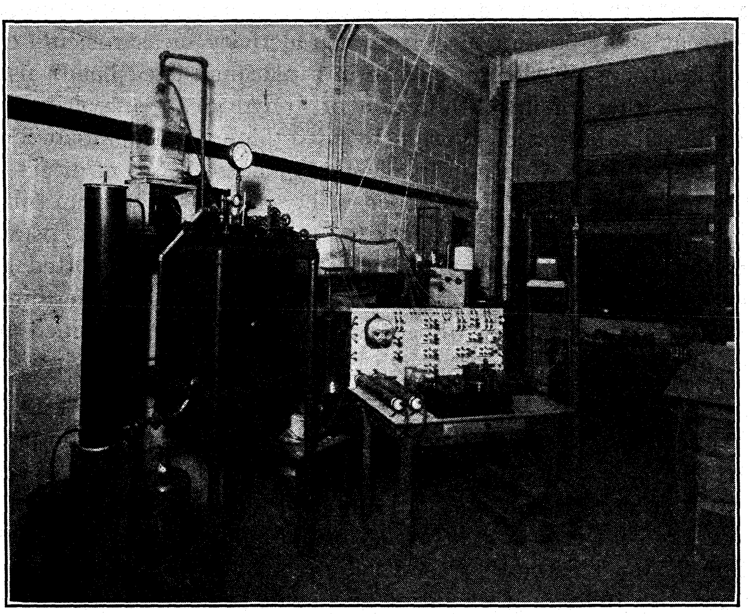


Fig. 3.—Equipment used in determining solubilities of calcium sulfate at temperatures above 100°C.

The *pump,* used for introducing solution into the boiler under pressure during an extended series of determinations, was loaned to the authors by Dr. R. E. Hall. It has previously been described by him elsewhere.[16]

The *internal filter* consisted of fifteen layers of very finely-woven cotton cloth supported between fine copper gauze and perforated metal plates and mounted in a cylindrical cup. Since this was mounted vertically within the boiler, a deposit of solid material accumulated in the cup during each run and served not only as an additional filter medium but also as a safeguard against the passage of supersaturated solution.

The *cooling coil* was made from twenty feet of $^1/_8''$ galvanized iron pipe bent in a spiral and suspended in a container through which tap water was rapidly circulated. The flow of solution samples was continuously downward from the internal filter to the discharge from the cooling coil. This discharge was regulated by a small needle valve just above the outlet.

---

[16] R. E. Hall and others, *Carnegie Inst. of Tech. Bull.,24,* 145 (1927).

The measurement of temperatures was carried out with copper–nickel thermocouples, since it was necessary to use this pair of elements in the scale formation tests also conducted in this boiler. For the solubility work the temperatures of the solution within the boiler and of the air thermostat were measured with a Leeds and Northrup Type K potentiometer and a galvanometer of the enclosed lamp-and-scale type, using ice in a thermos bottle for a cold junction. The thermocouples used were calibrated directly against a standardized thermometer in the vapor of boiling liquids. Distilled water, ethylene bromide, bromobenzene, aniline and nitrobenzene were used to establish the calibration curve between 100 and 200°. This curve was almost a straight line, with a slight concavity downward.

Experimental Procedure.—During the early part of the solubility determinations it was discovered that hemihydrate remained apparently stable for periods up to forty-eight hours when held at temperatures between 100 and 130° but at temperatures above the latter value the solubility values gradually dropped toward the anhydrite curve. In the neighborhood of 200" this change took place within a few hours. Advantage was taken of this natural establishment of equilibrium with anhydrite in determining the solubility curve for this form, instead of using a solid phase of anhydrite prepared by the ignition of gypsum.

At the start of each series of determinations, the boiler was filled with 10 liters of a solution saturated with respect to gypsum at room temperature, with a concentration very close to 2000 parts per million of $CaSO_4$. Ten grams of gypsum powder was introduced with the solution. The air thermostat was heated up to the temperature at which the first sample was to be taken and temperature readings were taken at occasional intervals until the boiler solution had become constant at this value. The first samples were taken at from two to twelve hours after this attainment of the steady state, longer intervals being used in the later series of determinations. Second samples were taken after a similar interval and in some cases third samples after another interval. The temperature of the air thermostat was then changed and the same procedure repeated at the new temperature. When the solution level in the boiler had dropped to that of the internal filter, a fresh charge was pumped in. During the early runs the stock solution of saturated calcium sulfate solution was used for refilling; during the later runs, distilled water, because it was found by experience that less time was lost in coming to equilibrium from a condition of undersaturation than from one of supersaturation. This was particularly noticeable in the case of determinations with anhydrite, so that points for this curve were obtained with successively decreasing temperatures in order to prevent the possibility of supersaturation.

Duplicate 250-cc. portions of solution were obtained at each sampling. The temperature of the cooled sample was measured and always fell between 14 and 16°. From this temperature and the calibration for the volumetric flask used in measuring the samples, the mass of the sample was obtained. The sample and the washings from the volumetric flask were acidified with 0.5 cc. of concentrated hydrochloric acid, and were evaporated on a hot-plate to a volume of approximately 200 cc. The sulfate was then precipitated with 20 cc. in excess of the calculated amount of a solution of barium chloride containing 20 g. per liter of $BaCl_2 \cdot 2H_2O$. The solution then was returned to the hot-plate and again evaporated to 150–200 cc. (one to two hours). It was then filtered through an alundum crucible and the precipitate was washed thoroughly with hot water. The crucible was ignited in an electric muffle furnace at approximately 850° for one hour and was cooled in a desiccator

Experimental Data and Discussion

The experimentally determined solubilities are given in Table I. Values representing pre-equilibrium conditions at various temperatures have been omitted, as have been values representing transition from hemihydrate to anhydrite in the range above 130°. The data of Table I are presented also in Fig. 2 as the solid circles. From Fig. 2 it is readily evident that the data of the authors for the hemihydrate curve check excellently with

TABLE I

EXPERIMENTAL SOLUBILITY DATA

Run no.	Time at temp., hrs.	Temp., °C.	Sol., parts per million	
			Hemi-hydrate	An-hydrite
1	10.0	144.3	620	
2	10.5	100.8	1709	
	4.0	119.4	1088	
	10.0	119.8	1072	
	9.0	123.2	976	
	10.0	123.2	972	
	2.5	131.2	835	
	1.0	132 7	827	
	3.0	142.2	645	
	4.0	142.2	644	
	4.5	145.8	590	
	1.0	148.9	532	
	3.0	148.9	535	
	3.0	163.3		167
3	1.0	100.3	1666	
	5.0	100.3	1640	
	1.5	101.3	1690	
	2.5	101.4	1690	
	3.0	127.8	902	
	12.0	140.1	683	
	3.0	146.6	586	
	6.0	195.2		76
	2.0	197.9		73
	4.0	197.6		65
4	11.0	98.5	1648	
	11.0	98.5	1640	
	2.5	100.3	1667	
	2.5	100.3	1667	
	16.0	112.7	1182	
	16.0	112.7	1178	
	4.0	115.5	1175	
	4.0	115.5	1177	
	8.0	135.1	745	
	8.0	135.1	744	
	2.5	170.5		150
	2.5	170.5		150
6	10.5	112.4	1217	
	10.5	112.4	1216	
	22.5	112.5	1198	
	22.5	112.5	1202	
	34.5	112.9	1179	
	34.5	112.9	1177	
	9.0	114.0	1117	
	9.0	114.0	1119	
6	1.5	197.0	139	
7	2.5	193.8		98
	2.5	193.8		102
	1.5	180.0		119
	1.5	180.0		114
8	4.5	195.2		80
	2.0	198.2		79
	6.5	184.5		111
	6.5	184.5		114
9	4	198.4		80
	4	198.4		74
10	18	197.9		76
	18	197.9		83
	10	185.6		101
	10	185.6		102
	24	184.2		105
	24	184.2		93
	8	169.6		152
	8	169.8		136
	9	169.5		137
	9	169.5		140
	20	169.6		137
	22	153.9		201
	22	153.9		206
	12	108.0		555
11	11	197.6		94
	11	197.6		64
	12	98.6		677
	12	98.6		677
	9	130.0		362

the previously published values of Boyer-Guillon, Melcher, and Hall, Robb and Coleman. In the case of the anhydrite curve, however, the authors' points check identically with those of Melcher and determine a curve which falls 200 parts per million below that of Hall, Robb and Coleman at 100°, approaching the latter as the temperature increases, until they attain an identical value at 200°.

It is the belief of the authors that the lowest points obtained by Hall, Robb and Coleman at each temperature for the solubility of anhydrite represent the most accurate determinations, and that the higher values indicate that complete conversion to anhydrite was not obtained in the preliminary burning of gypsum for their experiments. The variation between different determinations at the same temperature is easily accounted for by the assumption that varying amounts of hemihydrate were still present in the anhydrite added to their experimental boiler as the solid phase. This assumption is supported by the note appearing in their data to the effect that crystallographic examination of the solid phase from their boiler during one experiment showed material with refractive indices between 1.550 and 1.600. The alpha index of hemihydrate has been determined as 1.550, while the alpha index for anhydrite, its lowest index, is 1.571.[17]

At this time it is not possible to define with certainty the equilibrium diagram for the various forms of calcium sulfate in contact with water. The authors suggest the system shown in Fig. 4, in which the solubility curves of Figs. 1 and 2 are combined. Use has here been made of a solubility value for anhydrite at 33° given by Haddon and Brown,[18] which indicates the course of the anhydrite curve below 100°. This portion of the curve requires accurate determination before the intersection of the anhydrite and gypsum curves can be known with any certainty, but at present it appears to be at 38–39", which is the maximum of the gypsum solubility curve.

The transition temperature from gypsum to anhydrite given by van't Hoff[19] is 66". This value was obtained by two separate methods, one depending on vapor pressure and dilatometer measurements on concentrated salt solutions containing calcium sulfate, the other depending on a thermodynamic treatment of solubility data. The latter method is in error, since the solubility data of Boyer-Guillon were used under the misconception, common at the time, that they referred to anhydrite. The former method presents experimental difficulties which made van't Hoff consider it less certain than the latter. This transition temperature of 66°, therefore, is not securely founded.

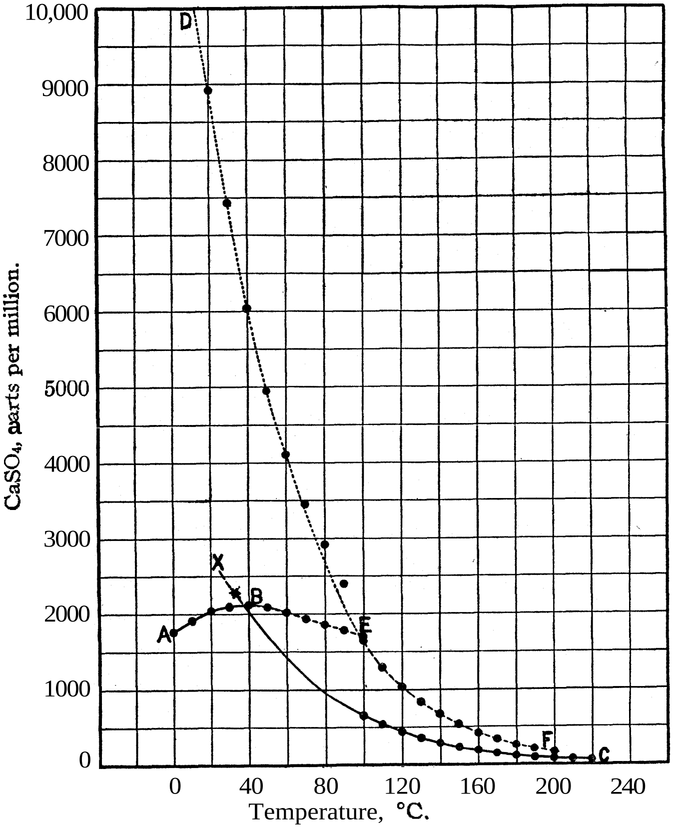
---

[17] E. S. Larsen, *Proc. Am. Soc. Testing Materials*, 23, 236 (1923).

[18] G. L. Haddon and M. W. A. Brown, *J. Soc. Chem. Ind.*, 43, 11–16T (1924).

[19] Van't Hoff and others, *Z. physik. Chem.*, 45, 257–306 (1903).

From work of the authors on calcium sulfate scale formation, which will be described in the future, it appears that while anhydrite should apparently be the stable solid phase formed from solution over the whole range of boiler temperatures, hemihydrate is actually formed in the range of 100–130°. This apparent anomaly requires further study, as does the fact that gypsum is not converted to anhydrite when in contact with water between 39 and 98" but does change rapidly to hemihydrate at some temperature between 98 and 100°. Incomplete experiments indicate that hemihydrate is converted very slowly to anhydrite at this latter temperature.



●, From Figs. 1 and 2; *, Haddon and Brown. ABE, gypsum, $CaSO_4{\cdot}2H_2O$; DEF, hemihydrate, $CaSO_4{\cdot}{}^1/_2\,H_2O$; XBC, anhydrite, $CaSO_4$.

Fig. 4.—Equilibrium diagram of the system calcium sulfate-water at temperatures from 0–220°C.

Table II gives the values at 10-degree temperature intervals of the solubilities of hemihydrate and of anhydrite in the range from 100 to 220". These values are taken from the curves of Fig. 2.

TABLE II

SOLUBILITIES OF HEMIHYDRATE AND ANHYDRITE AT ROUNDED TEMPERATURES FROM 100 TO 220°

Temp., °C.	Sol. as parts of $CaSO_4$ per million parts of soln. Hemihydrate	Anhydrite	Temp. °C.	Sol. as parts of $CaSO_4$ per million parts of soln. Hemihydrate	Anhydrite
100	1645	650	170	325	140
110	1290	535	180	255	112
120	1030	435	190	205	92
130	830	350	200	165	76
140	665	280	210	..	64
150	530	222	220	..	55
160	415	176			

Conclusions

The solubilities of hemihydrate and of anhydrite have been studied in the temperature range 100–200°. The values for the solubility of hemihydrate check those of earlier investigators commonly referred to as the values for the solubility of "soluble anhydrite." The values found for anhydrite are lower than the accepted values up to 200°, approaching the latter with increase in temperature and coinciding with them at 200°.

The solubility curve previously designated as that of "soluble anhydrite" between 100 and 200" has been shown to be a prolongation of the solubility curve for hemihydrate below 100°. Evidence that "soluble anhydrite" is identical in crystal structure with calcium sulfate hemihydrate has been advanced by other investigators and support of this view will be presented in a future paper by L. S. Ramsdell and E. P. Partridge.

A tentative equilibrium diagram for the system calcium sulfate–water is proposed, which indicates that the temperature of transition from gypsum to anhydrite lies slightly below 40° and that the temperature of transition from gypsum to hemihydrate lies at 98°.

Hemihydrate exists in contact with water only as an unstable phase over the entire temperature range 0–200°. In the range 90–130°, however, it is apparently metastable for periods up to forty-eight hours. Incomplete experiments indicate that gypsum is converted into hemihydrate in less than one day when in contact with water at 100°, and that the hemihydrate thus formed is subsequently transformed into anhydrite over longer periods of time.

Summary

Values for the solubility of calcium sulfate between 100 and 200° have been redetermined. The whole system of calcium sulfate and water up to 200° has been reviewed, with the conclusion that gypsum and anhydrite are the only stable phases within this range. The transition temperature of gypsum into anhydrite lies near 40°. Hemihydrate is the only other

form of calcium sulfate which has existence in the range 0–200°. "Soluble anhydrite" is identical in crystal form with hemihydrate, and the solubility curve formerly given as that of "soluble anhydrite" is the curve for hemihydrate. Hemihydrate is metastable in the approximate range 90–130°, showing decreasing stability with decrease of temperature below 90° and with increase of temperature above 130°.

ANN ARBOR, MICHIGAN

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

OXIDATIONS PROMOTED BY ULTRASONIC RADIATION

By F. O. Schmitt,[1] C. H. Johnson and A. R. Olson

Received August 13, 1928 Published February 5, 1929

During the course of an investigation of the effects of ultrasonic radiation on certain photosensitive reactions, it was found that iodine was liberated from an aqueous solution of potassium iodide by such radiation. It was subsequently discovered that other reactions were sensitive to this agency; indeed Richards and Loomis,[2] using a 2-kilowatt oscillator, have reported two cases in which they observed some stimulation.

Experimental Methods

The high-frequency mechanical vibrations were generated in a manner already described.[3] The electrical oscillations were produced by a single 250-watt tube tuned to the natural frequency of the quartz crystal, which was about 750 kilocycles per second. In the cases of almost all reactions reported in the present paper, the reactants were contained in a test-tube dipping into the liquid dielectric immediately over the crystal. In this way the energy was transmitted to the solution in the test-tube, resulting in vigorous cavitation of any dissolved gas, the escaping bubbles being momentarily caught in the nodes of the standing wave system. In certain reactions it was desirable to render the liquid free, to all practical purposes, of dissolved gases before radiation. This was accomplished by boiling for three or four minutes in a test-tube fitted with a valve. On cooling the tube the valve closed, excluding the air indefinitely. In other reactions in which the presence of only one gas was desired, the liquid was rendered air-free in the manner already described; the valve was removed and a layer of mineral oil laid over the surface; the gas to be dissolved was then bubbled in from a fine jet. The use of oil had certain disadvantages and it was never employed unless absolutely essential. In order to ascertain whether electrical oscillations were responsible for the observed effects, a test-tube containing the reactants was placed above

---

[1] Fellow in Medicine of the National Research Council.

[2] Richards and Loomis, This Journal, 49, 3086 (1927).

[3] Schmitt, Olson and Johnson, Proc. *Soc. Exptl. Biol.* Med., 25, 718 (1928).

the dielectric, another test-tube within the induction coil and a small receptacle containing potassium iodide and starch solution was inserted between the electrodes and the circuit tuned. In none of these experiments was any reaction observed, although the solutions within the induction coil, and between the electrodes, became hot.

Reactions Involving Gases

I. Oxidation of Halide Ions.—The oxidations of halide ions in neutral solutions by atmospheric oxygen in the dark are extremely slow reactions. If a 1 N aqueous solution of potassium iodide saturated with air under atmospheric pressure is subjected to ultrasonic radiation, iodine is liberated. When potassium iodide–starch reagent is added to aqueous solutions of potassium bromide and potassium chloride which have been radiated in the same way, the starch–iodine color appears immediately; if distilled water is radiated and tested in this manner no color appears until after a lapse of four or five minutes. Either the bromide and chloride ions are oxidized in these experiments or some other substance is produced in the presence of these salts which oxidizes the iodide ion instantaneously. To test the influence of positive ions 1 N potassium nitrate and 1 N potassium sulfate solutions were treated as above. Both of these solutions behaved essentially like distilled water but the rates of development of color were noticeably faster. To test further the influence of the positive ions, the above experiments were repeated with 1 N solutions of sodium and lithium salts and precisely similar results were obtained. Since Li^+ is considered to be highly hydrated in solution, the effect of hydration appears not to be important. It was also demonstrated that the hydrogen-ion concentration has a marked influence upon the rate and extent of color production. Although the halides showed an immediate color upon adding the starch–iodide reagent, the intensity of color developed by these solutions on standing in the dark for half an hour was as follows: $I^- > NO_3^- > SO_4^{--} > Cl^- >$ water $> Br^-$.

The depth of color produced by a three-minute period of radiation of potassium iodide solution is of the same order of magnitude as that produced by one part in a million of hydrogen perioxide. To test for the formation of hydrogen peroxide, titanium sulfate reagent was irradiated. Positive results were obtained in the majority of the trials; all of these solutions were sensitive to one part of hydrogen peroxide in three million parts of water. The formation of ozone was also suspected and it was tested for with manganous sulfate in acid solution. The tests were negative, but it is likely that this method is not sufficiently sensitive to justify the conclusion that no ozone was formed.

It is well known that the presence of ions influences the sensitivity of the starch–iodide test. Very dilute solutions of hydrogen peroxide were therefore added to starch–iodide reagent containing potassium salts. When potassium iodide was the salt added, a distinct color appeared immediately; with other salts a lapse of from one to three minutes occurred before color developed. The relative rates of color production in these experiments, under comparable conditions, were as follows: $I^- > NO_3^- > SO_4^{--} > Cl^- >$ water $> Br^-$. On standing in the dark for half an hour these solutions showed approximately the same depth of color although exhibiting some differences in shade.

The influence of the sulfate and nitrate ions in the case of the radiated solutions may merely have been upon the sensitivity of the starch–iodide test; but the immediate apppearance of color with bromide and chloride, on addition of the reagent after radiating, indicates some additional factor. This may be the production of free bromine and chlorine by oxidation of the halide ions.

2. Oxidation of Hydrogen Sulfide.—Aqueous solutions containing. hydrogen sulfide and air, when radiated for a few minutes, become strongly opalescent due to the oxidation of the hydrogen sulfide to sulfur, the latter appearing in the form of a colloidal precipitate. An attempt was made to estimate the amount of hydrogen sulfide which was oxidized under the influence of a three-minute period of radiation, by determining the strength of a solution of sodium thiosulfate required to react with sulfuric acid and yield a solution of the same degree of opalescence as an average radiated sample. The assay indicated that three minutes' radiation caused the oxidation of about 0.2 cc. of hydrogen sulfide gas, under standard conditions, from 5-cc. samples of solution. In this case, again, the rate of oxidation of an aqueous solution of hydrogen sulfide to sulfur by air alone is a reaction which even over a period of days does not proceed to any appreciable extent. A mixture of equal volumes of a 3% solution of hydrogen peroxide and of the aqueous solution of hydrogen sulfide produced opalescence at a much slower rate than that observed under the influence of ultrasonic radiation.

3. Oxidation of Organic Halogen Compounds.—A very striking result was obtained when a clear aqueous solution of carbon tetrachloride was radiated in the presence of starch and potassium iodide. The blue color of the starch iodide compound developed immediately; at the end of one minute of radiation the tube was practically opaque and the color many times deeper than that obtained by three minutes' radiation of potassium iodide and starch alone. Air and water must both be present for this reaction to occur.

If a two-phase system, carbon tetrachloride and aqueous potassium bromide solution, is radiated, the aqueous phase quickly becomes yellow due to the liberation of bromine. A number of other experiments involving organic compounds are now in progress and the results will be communicated in a later paper.

4. Reduction by Gaseous Hydrogen.—A solution of ferric ion through which hydrogen had been passed for a sufficiently long time to remove the dissolved air was radiated for five minutes. The resulting solution was tested for ferrous ion by potassium ferricyanide, and also for a change in the ferric-ion concentration with ferrocyanide and thiocyanate. In the most carefully controlled experiments no reduction could be detected. Had the amount of reduction been comparable to the amount of oxidation found in the former experiments, these tests would have been sufficiently delicate to detect the change.

Reactions not Involving Gases

Having succeeded in inducing reactions involving oxidations by oxygen under the influence of ultrasonic radiation, it next became necessary to determine whether slow reactions which proceed in the absence of oxygen could similarly be accelerated. Two reactions have already been studied by Richards and Loomis,[2] namely, the hydrolysis of dimethyl sulfate, and the iodine "clock" reaction, and the conclusion drawn that; after controlling the reactions as carefully as possible for differences in integral temperatures, there was a residual difference in rates which indicated that the radiation produced a 10% acceleration.

In certain of our experiments along quite different lines, in which Brom Thymol Blue was used and apparently positive results were obtained, it was suspected that the indicator itself was affected rather than that the reaction had been stimulated. Subsequent tests showed 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 changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of alkali caused a prompt return of the blue color. Other indicators, such as Brom Phenol Blue and litmus were affected in a similar manner. Whatever the process may be, there is no doubt that dye molecules were altered by the radiation and gave rise to hydrogen ions.

In the experiments of Richards and Loomis on the hydrolysis of dimethyl sulfate, Brom Thymol Blue was used to indicate the course of the hydrolysis. Since, during radiation, a sufficient amount of this indicator is decomposed to affect the color of the remaining indicator molecules, it follows that their results are not yet complete enough to justify their conclusions. We have shown above that if an aqueous solution con-containing dissolved oxygen is radiated, hydrogen peroxide or something analogous to it is formed. This must contribute to the acceleration of the iodine "clock" reaction observed by Richards and Loomis. Since the solutions employed by them were acid, any hydrogen peroxide produced by the radiation would transform the iodate to iodine independently of the mechanism of the "clock" reaction.

It will be shown in a later section of this paper that considerable importance must be attached to the cavitation of a gas from the reacting solutions. Consequently, all solutions at present under consideration were kept free of gases during the course of the reaction. In order to maintain the same sensitivity of test as in the previous experiments, all the reactions chosen involved the oxidation of iodide ion. Briefly, starch–iodide solution was added to three oxidizing agents, chlorate, arsenate and nitrite ions, respectively, in acid solution. Manipulation of the ionic concentrations and of P_H values permitted suitable regulation of the rates of oxidation. After mixing, the solutions were rendered free of gases and subjected to radiation, a control tube similarly treated but not radiated being kept in each experiment. The results can be summarized as follows. The oxidation of iodide ion proceeded slowly in all cases but in none of the experiments was it possible to state definitely that an increase in the reaction rate occurred, as a result of from five to fifteen minutes of radiation. Moreover, cavitation of nitrogen from solution during the course of the reactions produced no appreciable acceleration, It is evident that if any stimulation of these reactions occurred, the amount of such stimulation was small compared to that observed when oxygen was present.

The Effect of Pressure.—It is probably significant that the reactions which have been accelerated by ultrasonic vibrations have involved at least one gas. The oxidation of hydrogen sulfide presents the most striking example of stimulation and in this case both reactants are gases under normal conditions. To ascertain whether the oxidation occurred during the process of cavitation, on the assumption that the formation of an interface is essential to the activation of the oxygen molecules, experiments were carried out with aqueous solutions of potassium iodide containing very small amounts of dissolved air. Iodine was liberated although no bubbles were seen. Moreover, bubbling oxygen in a fine stream during radiation through an aqueous solution of potassium iodide and starch, which originally was gas-free, did not give rise to color, apparently since none of the oxygen dissolved. If an aqueous solution of potassium iodide and starch is saturated with oxygen gas under four or five atmospheres of pressure and then released, no oxidation of iodide ion occurs. It seems necessary to assume that every phase of bubble formation is realized in this process, and it must be concluded, therefore, that the mere formation of bubbles in the absence of ultrasonic vibrations is unable to effect the oxidation.

On the other hand, if solutions of potassium iodide or of hydrogen sulfide containing air were radiated for the same time at a series of increasing pressures, applied from an oxygen tank, it was found that the amount of reaction as measured by the depth of color or opalescence, respectively, slowly increased up to a certain pressure; above this critical pressure there was a sudden diminution in the reaction rate. The depth of color produced by three minutes' exposure increased somewhat with pressure, so that at a pressure of thirty-five pounds per square inch the color was definitely darker than at atmospheric pressure. Under these conditions no visible cavitation occurred during radiation. At fifty-five pounds the depth of color was still maintained, but on increasing the pressure pound by pound, a series of fainter and fainter colors was produced until at sixty-five pounds per square inch no color could be detected after three minutes' radiation. The critical pressure above which no measurable reaction takes place is an arbitrary figure depending chiefly upon the amount of dissolved gas and upon the intensity of radiation. In a series of experiments with very dilute hydrogen sulfide–air solutions, it occurred at twenty-seven pounds per square inch.

The fact that the color intensity increases slightly with pressure up to a certain point is to be expected. Increased pressure, the prevention of loss of reactants by cavitation, and the consequent minimizing of disturbances in the standing wave system produced by the larger bubbles all tend to augment the amount of reaction taking place during the period of radiation. The fact that higher pressures inhibit the reaction completely is a powerful argument against the hypothesis that individual oxygen molecules in solution can be activated directly by ultrasonic energy. A possible explanation of the phenomenon is that there exists a critical bubble size below the limits of visibility which is essential for the activation of the oxygen. Application of pressure beyond a certain amount prevents the cavitation of bubbles of this size and consequently inhibits the reaction. A pressure of seventy pounds per square inch does not affect the rate of oxidation of potassium iodide by hydrogen peroxide. The effect of pressure, therefore, must be on the rate of formation of hydrogen peroxide if this be the active agent.

It may be mentioned that the rise in temperature caused by exposing a test-tube containing 10 cc. of water at room temperature to three minutes of radiation was about 5°, both under atmospheric pressure and under an applied pressure of seventy pounds per square inch. In the latter case cavitation of air was prevented, and the piling up of the water at the meniscus noticeably increased. Yet, as stressed above, oxidations did not occur under these circumstances.

Summary

A number of substances in the presence of oxygen and water have been oxidized by subjecting them to ultrasonic radiation under such conditions that gas bubbles might be formed in the liquid.

BERKELEY, CALIFORNIA

[Contribution from the Department of Chemistry, Laboratory of Micro Analysis, Washington Square College, New York University]

GRAVIMETRIC METHOD FOR MICRO DETERMINATION OF MOLYBDENUM

By Joseph B. Niederl and Edith P. Silbert

Received August 17, 1928 Published February 5, 1929

Introduction.—As the necessity arose for determining molybdenum micro-analytically in organic compounds, it has been found that Pregl's method for the quantitative micro determination of metals in organic substances[1] can be used in principle for the gravimetric micro determination of molybdenum as molybdenum trioxide.

Apparatus.—While the apparatus and manipulations in the course of the analysis remained the same, the following changes were necessary in the analytical procedure to give satisfactory results.

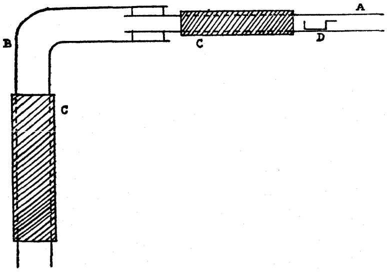


Fig. 1.—Micro muffle, according to Pregl. A, combustion tube; B, bent tube; C, wire gauze; D, combustion boat.

Method.—Three to five mg. of the substance is weighed in a micro porcelain combustion boat (a platinum boat cannot be used since partial reduction of the molybdenum trioxide may occur) on a micro-analytical balance (Christian Becker micro-analytical balance proved to be satisfactory). To this a drop of concentrated nitric acid is added. The boat is then brought into the combustion tube of the micro muffle (as shown in the diagram above) and heating begun over a small wire gauze with a Bunsen burner at about 30 mm. distance from the combustion boat.

Within a few minutes the nitric acid and the fumes of the oxides of nitrogen will be driven off and the wire gauze and flame are moved directly under the boat. After heating the boat in this manner for about five minutes, the wire gauze is removed and the heating continued at the same spot under the combustion boat for exactly five minutes longer. Since the molybdenum trioxide is volatile at temperatures above 450°,[2] the temperature of the flame is important. The flame should be non-luminous and so adjusted that it burns quietly, with an outer cone of about 7 cm. and an inner cone of about 3 cm. in length.

The material in the combustion boat should now appear yellow while

---

[1] F. Pregl, "Quantitative Organic Analysis," P. Blakiston's Son & Co., Philadelphia, 1924.

[2] W. D. Treadwell, Z. Elektrochem., 19, 219 (1913); Brinton and Stoppel, This Journal, 46, 2454 (1924).

hot and grayish-white when cold. At this point the operation is finished and the boat containing the molybdenum trioxide is weighed.

This method, which requires only a short time for completion, is applicable for organic and inorganic substances provided they contain no other non-combustible or non-volatile constituents.

Results.—Some of the results obtained are as follows.

Molybdic Acid. 56.67% of Molybdenum. Macro Analysis.

Sample taken, mg.	3.105	2.275	2.442	3.250
MoO_3, mg.	2.642	1.934	2.075	2.758
Molybdenum found, %	56.71	56.68	56.62	56.58

Ammonium Molybdate. 53.87% of Molybdenum. Macro Analysis.

Sample taken, mg.	4.155	5.675	3.786	2.667
MoO_3, mg.	3.339	4.576	3.045	2.144
Molybdenum found, %	53.57	53.75	53.53	53.59

Histamine Molybdate. Calcd., 48.24% of Molybdenum.

Sample taken, mg.	3.936	5.017	4.406
MoO_3, mg.	2.852	3.664	3.202
Molybdenum found, %	48.30	48.60	48.45

Summary

A rapid gravimetric micro method for the quantitative determination of molybdenum in organic compounds has been described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF MICHIGAN]

I. PURIFICATION OF METHYL FLUORIDE
II. QUANTITATIVE GAS ANALYSIS BY HIGH DISPERSION INFRA-RED SPECTROSCOPY

BY WILLARD H. BENNETT

RECEIVED AUGUST 20, 1928 PUBLISHED FEBRUARY 5, 1929

Besides the interest in a ready method for preparing pure methyl fluoride, it is thought that this investigation will be of interest inasmuch as an application of infra-red spectroscopy is made in determining the purity of an organic compound with greater accuracy than is available through the usual chemical methods.

The best method for the preparation of methyl fluoride which a search of the literature revealed was that of E. Moles and T. Batuecas.[1] They prepared silver fluoride by recrystallization and warmed with methyl iodide, purifying the vapors by repeated warming with silver fluoride. Their test of purity consisted of bringing the methyl fluoride gas to constant density by purification. They also tried the method of heating

---

[1] Moles and Batuecas, *J. chim. phys.*, 17,537 (1919).

potassium methyl sulfate with potassium fluoride and found that by the density determination method, they obtained 95% methyl fluoride at first, and then successively less methyl fluoride with each preparation, so the method was abandoned. It was stated that in all probability the impurity was methyl ether.

This investigation began with an attempt to find a method for the elimination of the methyl ether from the methyl fluoride prepared by the latter method, since the crystallization of silver fluoride is such a time-consuming operation.

Erlenmeyer and Kriechbaumer[2] give a method of preparation of methyl ether. Methyl alcohol is heated with concentrated sulfuric acid and the gas evolved is passed into concentrated sulfuric acid, which absorbs 600 volumes of methyl ether. This sulfuric acid solution is run into an equal volume of water, when 92% of the methyl ether is recovered. It was thus thought that concentrated sulfuric acid would be a good absorbent of methyl ether.

Potassium fluoride hydrate, $KF \cdot 2H_2O$ (Baker), was heated until the water of crystallization had boiled off, leaving a white mass of anhydrous potassium fluoride, KF. This was pulverized. Potassium methyl sulfate, crystalline KCH_3SO_4 (Eastman), was pulverized and mixed with the pulverized potassium fluoride in the ratio of two parts of KF to five parts of KCH_3SO_4. The mixture was heated to 140–200°. The gas evolved was passed (1) through concentrated sulfuric acid in a spiral wash bottle with a gas path of about 65 cm., (2) through a concentrated solution of potassium hydroxide, (3) through a drying tube of soda lime and two drying tubes of calcium chloride (fused), and (4) into a condenser submerged in liquid air.

Methyl fluoride is solid at the boiling point of liquid air, so care had to be exercised to keep solid methyl fluoride from plugging the entrance tube to the condenser bulb. The middle fraction was taken from the methyl fluoride boiling out of the condenser on lifting the latter from the liquid air.

The impurities to be expected from reactions occurring in heating $KF + KCH_3SO_4$ are CO_2, H_2O, $(CH_3)_2O$, C_2H_4 and SO_2. The KOH is known to absorb CO_2 and SO_2 quantitatively, and $CaCl_2$ absorbs the H_2O.

Three samples of methyl fluoride were prepared. Sample A was prepared by removing the sulfuric acid bottle from the purification train, the gas being passed into the spectroscopic absorption cell without condensing with liquid air. Sample B was made without the sulfuric acid bottle also, but it was fractionated from liquid air. Sample C was prepared pure as above described.

The spectra of these three samples were measured on the high dispersion spectrometer in this Laboratory. A fairly large range of wave length of the radiation from a Nernst glower was selected by a fore-prism spectrometer. This radiation was passed through the gas cell and allowed to fall on the entrance slit of the grating spectrometer. A Michigan echelette grating ruled on a solder surface with 1440 lines per inch was used to further disperse the beam. The exit slit selected a narrow range of wave length of radiation which fell on a junction of a Pfund thermopile. The current from the thermopile was amplified by means of a Moll-Burger thermo-relay. The current from this relay was measured by means of a high sensitivity Leeds and Northrup galvanometer.

---

[2] Erlenmeyer and Kriechbaumer, *Ber.*, 7,699 (1875).

The gas cell was built of brass and was provided with rock salt windows. It was sealed so that the rise of pressure, after evacuation, was about 0.1 mm. in the course of two days. A pump, a manometer and a McLeod gage were used for controlling and measuring the pressure of gas used in each spectroscopic measurement.

A more detailed description of the apparatus and of the method of observation is being published concurrently with this.[3]

A preliminary inspection of the spectra when plotted showed that samples A and B contained methyl ether but that sample C contained practically none of the ether. The spectra of none of the samples showed any similarity to the spectrum of the band in this region for ethylene, so it was definitely concluded at the outset that none of the latter gas was present.

In a previous communication[4] the variation of infra-red absorption in liquids with cell thickness was studied and it was found experimentally that for small cell thicknesses the absorption is approximately proportional to the thickness. Since the fine structure of the spectrum of the methyl ether is not resolved with the slit width used, the absorption of the gas will vary with gas concentration in the cell in the same manner that it does with cell thickness in the case of liquids, and the percentage absorption will be porportional to the gas concentration for small percentage absorptions, to within the accuracy of these measurements. The validity of this assumption was checked by measuring the spectrum of pure methyl ether at 2 cm. and 4 cm. pressure, and the respective absorptions were found to differ by a factor of 2, to within the experimental error stated later.

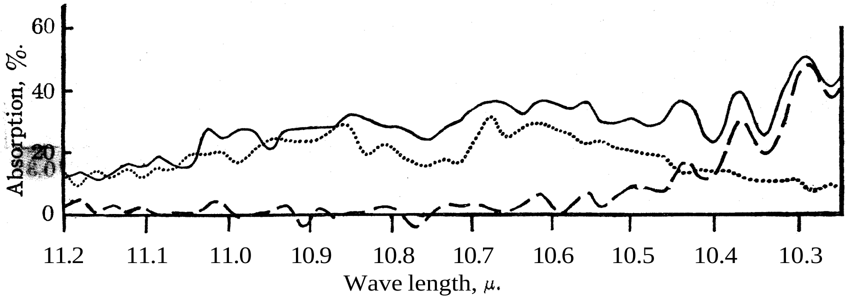


Fig. 1.

Fig. 1 shows the absorption spectra in the region 10.3 μ to 11.2 μ of these samples. No essential difference was found in the spectra of samples A and B and these, with the absorption cell filled at 73.6 cm. pressure, are shown as the full line. The spectrum of sample C at 73.7 cm. pressure

---

[3] Willard H. Bennett and Charles F. Meyer, "The Infra-red Absorption Spectra of the Methyl Halides," Phys. *Rev.*, **32,** 888 (1928).

[4] Willard H. Bennett and Farrington Daniels, THIS JOURNAL, 49, 50 (1927).

is shown as the broken line and the spectrum of methyl ether at 2.0 cm. pressure is shown as the dotted line. Fig. 2 shows that part of the 10-p

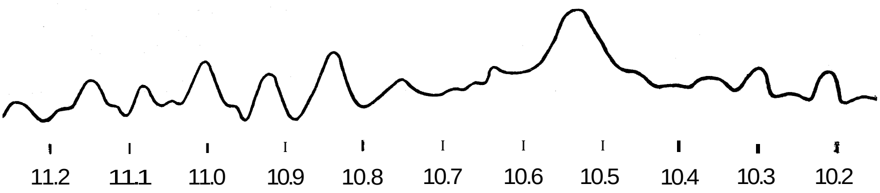


Fig. 2.

band for ethylene at a low pressure which lies in this region.[5] In Fig. 3, the full line represents the observed absorption percentages for the purified methyl fluoride at 73.7 cm. pressure. The dotted line represents the absorption of the empty cell.

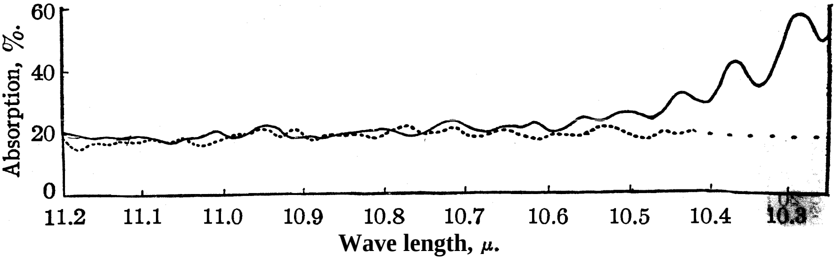


Fig. 3.

From data compiled in Table I, the percentages of methyl ether present in samples A and B were determined. The range of wave length from 10.8 μ to 11.2 μ was deemed the most representative. Readings were taken at 2' intervals of circle setting as given in Col. 1. Cols. 2, 3 and 4 give the percentages of absorption of samples A and B and methyl ether, respectively. Cols. 5 and 6 give the ratios of the absorption of methyl ether to the absorptions of samples A and B, respectively. By the method of least squares, the value of the ratios for samples A and B are 118 ± 4% and 123 ± 4%, respectively. Since the methyl ether spectrum was measured with the gas at 2.0 cm. pressure, while the spectra of samples A and B were both taken at 73.6 cm. pressure, the molar concentrations of methyl ether in samples A and B are

$$\frac{2.0}{73.6}\,(1.18 \pm 0.04) \text{ and } \frac{2.0}{73.6}\,(1.23 \pm 0.04)$$

or 3.08 ± 0.10% and 3.21 ± 0.10%, respectively. Hence fractionation from liquid air has not removed methyl ether to within the probable experimental error, which is 0.10%.

---

[5] A. Levin and C. F. Meyer, J. *Opt. Soc. Am.*, 16,137 (1928).

TABLE I
EXPERIMENTAL DATA

1	2	3	4	5	6
3830	12.0	13.5	13.5	89	100
28	13.5	14.0	9.5	142	147
26	12.5	16.5	14.0	89	118
24	13.5	16.5	12.0	112	137
22	16.5	16.0	14.5	114	110
20	15.5	15.5	12.0	129	129
18	18.5	16.0	15.0	123	107
16	15.5	18.0	14.5	107	124
14	15.5	18.0	19.5	80	93
12	27.5	22.5	19.5	141	115
10	24.5	24.5	20.0	122	122
8	27.0	26.0	16.5	163	158
6	26.5	27.0	21.0	126	128
4	21.0	27.0	24.0	88	112
2	27.0	29.5	24.0	112	123
38 0	27.0	32.0	23.5	117	136
37 58	28.0	31.5	24.0	117	131
56	27.5	30.0	27.5	100	109
54	32.0	31.0	27.5	116	113
52	30.0	28.0	19.0	158	147
50	28.0	29.0	22.5	124	129

Table II gives the data used in the computation of methyl ether present in sample C. As seen in Fig. 3, some values of the percentage absorption for the cell empty are greater than those for the cell filled with sample C. This is due to the experimental error in each reading. Giving the values in the same order as in Table I, Col. 1 gives the circle setting, Cols. 2 and 3 the absorption percentages for sample C and methyl ether, respectively, and Col. 4 the ratios of the corresponding percentages in Col. 3 to those in Col. 2. The value of the ratio by the method of least squares is 7.9 ± 3.0% and the molar concentration of methyl ether in sample C is 0.20 ± 0.08%. It is thus seen that it is possible but not probable that all of the methyl ether has been removed by washing with concentrated sulfuric acid.

TABLE II
EXPERIMENTAL DATA

1	2	3	4
3830	2.5	13.5	19
28	5.0	9.5	53
26	1.0	14.0	7
24	3.0	12.0	28
22	0.5	14.5	3
20	2.5	12.0	21
18	0.0	15.0	0
16	0.5	14.5	3
14	0.5	19.5	3
12	3.0	19.5	15
10	3.5	20.5	17
8	−1.0	16.5	−6
6	0.0	21.0	0
4	1.0	24.0	4
2	3.0	24.0	12
38 0	−3.5	23.5	−15
37 58	2.0	24.0	−8
56	−1.0	27.5	−4
54	0.5	27.5	2
52	0.5	19.0	3
50	3.0	22.5	13

Summary

1. A ready method for preparing methyl fluoride **pure** to within 0.20 ± 0.08% has been described.
2. Quantitative analyses of samples of this gas have been made by high dispersion measurement of the infra-red spectra of the samples, giving probable errors of 0.10%.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OB THE STATE UNIVERSITY OF IOWA]

OXIDATION–REDUCTION POTENTIALS. I. THE FERRIC–FERROUS ELECTRODE

BY STEPHEN POPOFF AND ADOLF H. KUNZ

RECEIVED AUGUST 23, 1928 PUBLISHED FEBRUARY 5, 1929

The two outstanding difficulties in the interpretation of oxidation–reduction potential half-cells are the incomplete elimination of liquid junction potentials and the lack of precise data on the activity of one electrolyte in the presence of one or more others. According to Gerke[1] the published data in this field abound with unnecessary liquid junction potential corrections which cannot be precisely computed.

In the present study of the oxidation–reduction potential of the ferric–ferrous half-cell the foregoing difficulties were reduced to a minimum. Electromotive force measurements were made of the cell

$$\mathrm{Pt, H_2 \mid HCl \mid HCl + FeCl_3 + FeCl_2 \mid Pt}$$

The liquid junction potential was kept constant by a Lamb and Larson[2] flowing junction. In each series the acid concentration was the same throughout the cell. In all cases the ratio of the concentrations of the ferric and ferrous chlorides was kept as nearly as possible equal to one.

With decreasing concentration of ferric and ferrous chlorides, within each series, both sides of the cell approach identity and the liquid junction potential approaches zero. By plotting a function of the potential against the concentration of the ferrous chloride and extrapolating to zero concentration, the liquid junction potential disappears.

To obtain the normal oxidation–reduction potential a correction must be made for the presence of the hydrochloric acid. This was accomplished by plotting the values derived from the graphs at various acidities against the acid concentration and again extrapolating to zero.

Special Equipment

1. Electrode Vessel.—An all-glass electrode vessel[3] shown in Fig. 1 was used for the potential measurements. A is the oxidation–reduction chamber in which were placed the mixtures of ferrous and ferric chlorides and hydrochloric acid. T is a platinum foil, 8 × 18 *mm.*, sealed into a glass holder which is filled with mercury for contact. S is a stirrer with a liquid seal in which was put some of the same solution as in A. L was not used in this problem. B is the hydrogen electrode chamber. E are duplicate platinum electrodes. F is the hydrogen inlet and G the outlet. In G was placed acid of the same concentration as in B. The two chambers are connected by a Lamb and Larson flowing junction H. C contained the same solution as A and C the same as B.

---

[1] Gerke, Chem. Reviews, 1, 388 (1925).

[2] Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

[3] Much credit for the design of this and other apparatus used is due to J. A. Riddick who was working on a similar problem.

The rate of flow is regulated by the overflow N. K and K' are stopcocks to prevent diffusion.

2. Constant Temperature Bath.—"White Rose" oil was used as the liquid in the bath. The temperature was easily kept at 25 ± 0.01°. The temperature was determined by a 0.1° thermometer which was compared with a similar thermometer calibrated by the Bureau of Standards. A Beckmann thermometer in the bath served as indicator for temperature changes.

3. Potentiometer and Galvanometer.—A Leeds and Northrup Type K potentiometer was used in conjunction with a Leeds and Northrup galvanometer, 2339a, and a lamp and scale reflector. A small lead storage cell was used for the working battery. The potentiometer and galvanometer were put on an equipotential base with the bath.

4. Standard Cell.—An Eppley standard cell of the unsaturated type was used. This was checked indirectly with a cell calibrated by the Bureau of Standards.

5. Oxygen Remover.—A 100-watt tungsten filament electric light bulb with sealed-in inlet and outlet tubes served to remove any possible traces of oxygen from the hydrogen used. The bulb was attached to a 110-volt circuit in series with a lamp-bank containing two 100-watt carbon bulbs in parallel.

Materials

1. All water used was redistilled from alkaline permanganate.

2. All hydrochloric acid was distilled twice from C. P. acid after dilution to a specific gravity of about 1.1.

3. Ferrous Chloride.—J. T. Baker's C. P. anhydrous salt was recrystallized twice from hydrochloric acid. Baxter and Hoover[4] found that two recrystallizations are sufficient to eliminate the predominating metallic impurities.

4. Ferric Chloride.—Chlorine was passed through a hot concentrated solution of the recrystallized ferrous chloride in hydrochloric acid. The ferric solution showed only a very faint and negligible test for ferrous iron. The chlorine was prepared in an all-glass vessel by adding redistilled hydrochloric acid to C. P. potassium permanganate.

5. Potassium permanganate was recrystallized twice for making the analyzing solutions.

6. Hydrogen was generated electrolytically from a concentrated solution of sodium hydroxide, using nickel electrodes. The gas was passed in order through a solution of potassium permanganate, an oxygen remover and three wash bottles (the last one was in the bath) containing acid of the same concentration as that in the hydrogen electrode vessel.

7. Silver nitrate, stannous chloride, mercuric chloride and preventive solutions were made from the best C. P. grade chemicals obtainable.

Analytical Methods

1. **Standardization of** 0.1 N Potassium Permanganate **Solution.**—Both iron wire and sodium oxalate were used. In the former case several lengths of bright iron wire containing 99.858% of iron were dissolved in 5 cc. of concentrated hydrochloric acid and 35 cc. of water and the solution boiled for five minutes to expel carbides. A drop of stannous chloride solution was added while hot. After cooling, 10 cc. of saturated mercuric chloride and 20 cc. of preventive mixture were added. After a short in-

---

[4] Baxter and Hoover, THIS JOURNAL, 34, 1660 (1912).

terval it was titrated electrometrically with potassium permanganate. In this and all other analyses titrations were made with weight burets. Results were also obtained without adding stannous chloride. In the sodium oxalate method the conditions of McBride[5] were followed. The results are presented in Table I.

It is evident that the titer increases with the amount of iron wire used, and that the value is higher when stannous chloride is used. Since subsequent work showed that the presence of mercurous chloride is objectionable the method without stannous chloride is probably the better, especially since it compares quite favorably with the sodium oxalate method.

TABLE I

THE STANDARDIZATION OF $KMnO_4$

	With Stannous Chloride			
G. of Fe	0.22590	0.22650	0.25460	0.25700
Fe titer	0.005802	0.005800	0.005824	0.005826
	Without Stannous Chloride			
G. of Fe	0.06310	0.06400	0.12580	0.12730
Fe titer	0.005765	0.005757	0.005781	0.005796
G. of Fe	0.12830	0.22150	0.22680	
Fe titer	0.005800	0.005807	0.005808	
	Using Sodium Oxalate			
Sodium oxalate titer	0.006974	0.006984		
G. of Fe per g. of soln.	0.005815	0.005815		

The absolute value of the iron titer of the potassium permanganate was not really required in this study as it deals principally with the ratio of the concentrations of the ferrous and ferric iron. Therefore it is only necessary that the permanganate be used under identical conditions in all iron titrations, ferrous as well as total.

2. Standardization **of** 0.01 N Potassium **Permanganate.**—This was accomplished by diluting to 0.01 N a solution of ferrous chloride whose total iron content had been previously determined with 0.1 N potassium permanganate. The 0.01 N ferrous chloride (after reduction of the ferric iron present) was titrated electrometrically with the dilute permanganate. No satisfactory electrometric end-point could be obtained when mercurous chloride was present so it was filtered off through asbestos before titrating. To be sure that no appreciable oxidation of iron takes place in filtering and transferring the ferrous solution, three drops of stannous chloride were added to 28 cc. of one molal hydrochloric acid containing 10 cc. of mercuric chloride solution. Twelve cc. of ferrous chloride solution in one molal acid was then added, the mercurous chloride filtered off and, after adding 20 cc. of preventive mixture, the solution was titrated. Fer-

---

[5] McBride, THIS JOURNAL, 34, 393 (1912).

rous chloride solution was titrated in the usual way at the same time. The results are shown in Table II.

TABLE II

OXIDATION OF Fe^{++} BY FILTERING

	G. of Fe per g. of soln.	Average
Filtering	0.019205, 0.019213	0.019209
Not filtering	0.019209, 0.019197, 0.019213	0.019206

3. Standardization of Silver Nitrate Solution.—This was done electrometrically using a silver chloride electrode with hydrochloric acid *as* the standard.

4. Standardization of Hydrochloric Acid Solution.—A carbonate-free solution of sodium hydroxide was prepared by adding a slight excess of barium hydroxide to an approximately 0.4 *N* solution of sodium hydroxide. This was filtered through asbestos out of contact with carbon dioxide and then standardized with benzoic acid and by hydrochloric acid diluted from constant boiling acid prepared by the method of Foulk and Hollingsworth.[6] The two methods agreed to within 0.05%. An error of 0.1% in the standardization of one molal acid will make an error of 0.06 mv. in the potential of the hydrogen electrode. The solution was kept in a paraffined bottle. After two months it showed no change. The acid solutions were standardized with this base, using phenolphthalein as the indicator.

5. The Determination of Ferrous Iron.—As the iron titer of a solution varies with the amount of acid present, enough acid was added in every titration to make a total of approximately 40 cc. of one molal hydrochloric acid. Twenty cc. of preventive mixture and enough water were added to make the volume at the close of the titration 200 cc. The titration was performed electrometrically.

That no appreciable oxidation of ferrous iron takes place during the time of titration is shown in Table III by comparing values obtained by titrating a solution containing ferrous iron (and about the same concentration of ferric iron) in one molal hydrochloric acid with 0.01 *N* potassium permanganate. As all titrations were made under these conditions, the air was not excluded.

TABLE III

COMPARISON OF Fe TITRATION IN AIR AND CO_2

G. of Fe per g. of soln.	In air	0.00052061	0.00052062
	In CO_2	0.00052061	0.00052074

When the ratio of ferrous and ferric iron is nearly one and the concentration of acid is about one molal, there is very little oxidation when left standing in a bottle half full of air. In one case there was no appreciable

---

[6] Foulk and Hollingsworth, THIS JOURNAL, 45,1220 (1923).

decrease in ferrous iron concentration overnight and less than 1% decrease in a week.

When the ratio of ferrous to ferric iron is greater than one, oxidation is slightly more rapid in one molal acid and considerably more rapid in solutions of lower acid concentration.

6. The Determination of Total Iron.—This was done in a similar fashion after reduction with stannous chloride and filtering off the mercurous chloride. The total iron content for the solutions employed (Tables II and IV) was about the same. That the filtering of the mercurous chloride is necessary is shown by the results in Table IV.

TABLE IV

INFLUENCE OF Hg_2Cl_2 ON TITRATION OF IRON

G. of Fe per g. of soln.	Filtered	0.016303	0.016298
	Not filtered	0.016320	0.016324

The difference of 0.15% between the filtered and non-filtered will cause a difference of 0.3% in the ratio of the concentration of ferrous to ferric iron. An error of 0.4% in the ratio will make an error of 0.1 mv. in the potential of the cell.

7. Determination of Total Chlorides.—This was done electrometrically with a silver chloride electrode as in the standardization of the silver nitrate solution. Table V shows a comparison between the chloride content of one solution determined by the electrometric method and by the Volhard method.

TABLE V

COMPARISON BETWEEN ELECTROMETRIC AND VOLHARDT METHODS FOR THE DETERMINATION OF CHLORIDES

Method	Volhard	Electrometric
G. of Cl per g. of soln.	0.05697, 0.05688	0.05704, 0.05706

The better agreement of duplicates and the rapidity of the electrometric method are strong arguments in its favor. Here again the exact value for the chloride content is not so important, for any error is minimized by dilution with accurately standardized acid.

Experimental Methods and Calculations

1. Hydrochloric Acid Solution.—The stock solution of acid was analyzed and the value recorded as grams of vacuum weight hydrogen chloride per gram of air weight of solution. This was diluted to the required molality by weighing out a definite quantity and adding the calculated weight of water, using the proper buoyancy correction factors. After dilution the solution was checked by another analysis and readjusted if not within 0.1% of the desired molality.

2. Ferrous Chloride Solutions.—The stock solution of ferrous chloride in hydrochloric acid was analyzed for ferrous iron, total iron and total chlorides. The ferric iron content was taken as the difference between the total and ferrous iron. The amount of water required to dilute the solution to the proper molality of acid was calculated and then added.

3. Ferric Chloride Solutions.—These were diluted to the same molality as the ferrous chloride solution and in the same manner.

4. Mixing Solutions to 1 : 1 Ratio of Ferric and Ferrous Iron.—The total iron content of the ferrous and ferric chloride solutions was calculated from dilution data. The ferrous content of the ferrous chloride solution was determined by titration just before mixing.

The ferrous-ferric mixture was made in the ratio of 0.998:1 in order to take care of a small amount of oxidation which takes place in the mixing and standing before use.

In Series V the 1:1 mixture was made up for each run and then diluted to the desired concentration of ferrous iron with one molal hydrochloric acid. After completing the potential measurements of the cells the ferrous iron of the solution of the cell was determined and the ratio of ferrous to ferric iron calculated. In all cases the ratio was within a few tenths of one per cent. of the value calculated for dilution.

In the other series a larger quantity of the I:1 mixture was made up, analyzed and kept in an atmosphere of carbon dioxide. The solution was analyzed before using for dilution and again the following day. Typical results are given in Table VI.

TABLE VI

THE STABILITY OR MIXTURES OR FERROUS AND FERRIC CHLORIDE IN AN ATMOSPHERE OR CO_2

G. of Fe per g. of soln.	Before use	0.011096	0.011095
	After use (one day)	0.011085	0.011093

That there is no appreciable oxidation of ferrous iron during the process of dilution is shown in Table VII.

TABLE VII

COMPARISON OF ANALYZED AND CALCULATED AMOUNTS OF Fe^{++}

G. of Fe per g. of soln.	Calculated	0.00023872
	Analyzed	0.00023870, 0.00023850

5. Calculation of Potentials.—There are three sources of potential in the cell

$$\mathrm{Pt, H_2} \underset{E_1}{\mid} \mathrm{HCl} \underset{E_2}{\mid} \mathrm{HCl + FeCl_2 + FeCl_3} \underset{E_3}{\mid} \mathrm{Pt}$$

E_1 is the potential of the hydrogen electrode, which is given by the equation

$$E_1 = -0.05915 \log a_{H^+}/a_{H_2} \qquad (1)$$

or

$$E_1 = 0.05915 \left(\tfrac{1}{2} \log p_{H_2} - \tfrac{1}{2} \log 760 - \log a_{H^+}\right) \qquad (2)$$

in which p is the partial pressure of the hydrogen of a solution of hydrochloric acid whose hydrogen-ion activity is a.

The values of Randall and Young[7] for the activities of hydrochloric acid were used. The partial pressure of the hydrogen was taken as the barometric pressure (corrected for temperature of barometer) minus the vapor pressure of the acid used. Values for the vapor pressures were calculated from data in "International Critical Tables."[8]

---

[7] Randall and Young, THIS JOURNAL, 50, 995 (1928).

[8] "International Critical Tables," 1928, Vol. III, p. 293.

E_2 is a liquid junction potential which cannot be computed at finite concentrations of ferrous and ferric chlorides. In the method of extrapolation used it disappears; hence it is included with E_3. E_3 is the potential of the ferric–ferrous electrode given by equation

$$E_3 = E_1 - E_{\text{cell}} \tag{3}$$

6. Experimental Details.—The hydrogen electrode vessels (Fig. 1) were filled to a level so that half of the platinized platinum electrode was immersed in the acid and the other half exposed to the hydrogen gas. The electrodes were platinized by the method of Popoff, Kunz and Snow[9] except that the treatment with nitric acid was omitted. Electrodes prepared with and without treatment with nitric acid agreed to within 0.01 mv. All duplicate electrodes prepared were within this agreement.

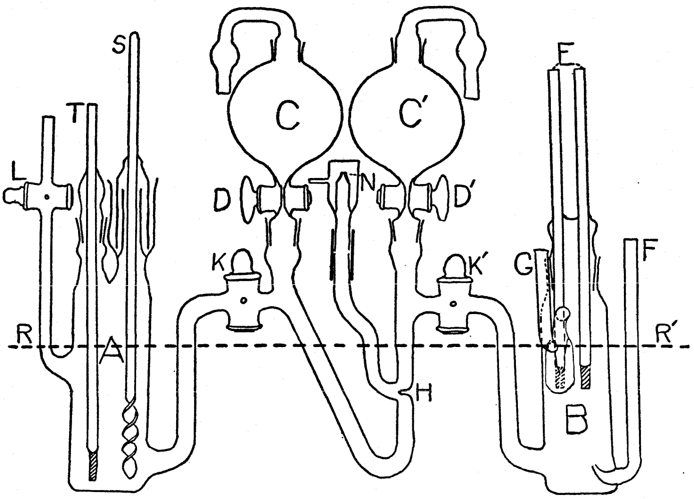


Fig. 1.—Electrode vessel.

In the previous investigation thinly and thickly plated electrodes were found to give the same potential to within 0.1 mv. The present study showed that the agreement is within 0.01 mv. However, the thickly coated electrode requires a longer time to attain equilibrium.

The oxidation–reduction half-cells were completely filled with the mixture of ferrous and ferric chlorides in hydrochloric acid. That no oxidation of the ferrous iron takes place in the cells was proved by analyzing the solution from duplicate cells, one at the end of one day and the other the following day. The variations of the results were within the limits of the experimental precision.

The cells were immersed in the oil of the bath up to line RR'. The rate of overflow from the flowing junction was about 300 cc. per hour.

Measurements of the electromotive forces of the cells were made about two hours after the hydrogen was admitted. Readings were then made about every half hour. After the cell readings did not differ for two hours the cells were assumed to be at equilibrium as cells left in overnight did not change their potential. In the fifth series Potential measurements were recorded to 0.01 mv. At the lower (0.2 to 0.05) concentration of acid the readings could only be obtained definitely to 0.05 mv. All observa-

---

[9] Popoff, Kunz and Snow, J. *Phys. Chem.,* 32,1056 (1928).

tions were made with stopcocks K and K′ closed. These were greaseless. No change in potential was caused by stirring the solution in the oxidation-reduction chambers.

Experimental Data and Discussion

1. The Oxidation–Reduction Potential at Various Acid Concentrations.—In Table **VIII** are presented the potentials of the ferric–ferrous electrode at various acid concentrations and with the ratio of the concentrations of the ferric and ferrous ion nearly equal to one. The data from which the potentials were calculated are also given. In every case there is a liquid junction potential (E_l) which decreases with dilution. The potential of the electrode, then, is expressed by the equation

$$E = E_0 - 0.05915 \log (a_{\text{Fe}^{+++}}/a_{\text{Fe}^{++}}) \pm E_l \qquad (4)$$

or

$$E_0 = [E + 0.05915 \log (C_{\text{Fe}^{+++}}/C_{\text{Fe}^{++}})] + 0.05915 \log (\gamma_{\text{Fe}^{+++}}/\gamma_{\text{Fe}^{++}}) \pm E_l \qquad (5)$$

TABLE VIII

THE OXIDATION–REDUCTION POTENTIALS

Cell	*Fe, mml. per 1000 g. of soln.*	Obs. e.m.f. of *cell*	E_a	*Cell*	*Fe, mml. per 1000 g. of soln.*	Obs. e.m.f. of *cell*	E_a
Series I (0.05 M Hydrochloric Acid)				Series IV (0.5 M Hydrochloric Acid)			
A	73.336	0.80550	−0.72449	A	71.963	0.72790	−0.70359
B	37.550	.80860	− .72759	B	36.301	.73065	− .70634
C	19.067	.81235	− .73137	C	18.291	.73255	− .70817
D	9.4312	.81470	− .73372	D	9.2493	.73340	− .70902
E	5.3184	,81695	− .73597	E	4.5286	.73375	− .70937
F	2.5539	.81815	− .73719	F	2.4826	.73395	− .70957
Series II (0.1 M Hydrochloric Acid)				Series V (1 M Hydrochloric **Acid)**			
A	19.191	.79020	− .72593	A	56.939	0.70042	−0.69642
B	9.3974	.79240	− ,72821	B	29.001	.70209	− .69801
C	4.7993	.79370	− .72949	C	12.412	.70313	− .69891
D	2.5977	.79440	− .73023	D	6.0924	.70353	− .69931
Series III (0.2 M Hydrochloric Acid)				E	3.4839	.70366	− .69967
A	17.847	.76665	− .71903				
B	8.8552	,76835	− .72073				
C	4.5451	,76900	− .72138				
D	2.2022	.76945	− .72183				

The values of the terms in the parentheses ([ ]) are called E_a in the tables. The factor 0.05915 log $(C_{\text{Fe}^{+++}}/C_{\text{Fe}^{++}})$ corrects for the small departure from a one to one ratio between the ferric and ferrous iron concentrations. Since the difference is very small it will not appreciably affect the ratio of the activity coefficients.

Fig. 2 shows the results of plotting the values of E_a at each acidity against the concentration of the ferrous iron and extrapolating to zero concentration at which E_l is eliminated. The extrapolated values (E_0') read from the graph are presented in Table IX.

Table IX

The Oxidation–Reduction Potential at Various Acid Concentrations

Series	I	II	III	IV	V
Molality of HCl	0.05	0.1	0.2	0.5	1.0
E_0'	−0.7386	−0.7311	−0.7222	−0.7098	−0.7000

It is suggested that these values of E_0' are of greater practical importance than the theoretical value of E_0 since in actual practice oxidation–reduction reactions involving iron are usually carried out in acid solution. Therefore in making predictions based on Equation 4 these values should be used.

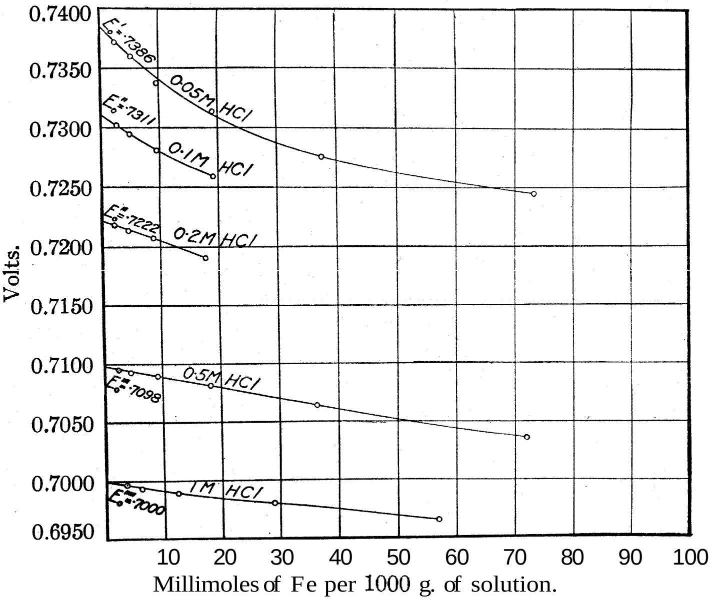


Fig. 2.—The oxidation–reduction potentials at various acid concentrations and with decreasing iron concentrations.

2. The Normal Oxidation–Reduction Potential.—In Fig. 3 the values of E_0' are plotted against the concentration of acid and the curve extrapolated to zero concentration. This corrects for the effect of the hydrochloric acid upon the activities of the ferrous and ferric ions and the normal oxidation–reduction potential of the ferric–ferrous electrode is found to be —0.7476 volt.

In Fig. 4 the logarithms of the values of E_0' are plotted against the acid concentration and extrapolated in the same way. This gives a somewhat better curve for extrapolation. The extrapolated value is 8.8737–10, whose antilogarithm is 0.7477.

3. Comparison between Results from Equilibrium and Electromotive

Force Methods.—Noyes and Brann[10] determined equilibrium constants at 25° for the reaction

$$Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2 \qquad (6)$$

at an acid concentration of 0.05 M nitric. By plotting the values obtained against the total nitrate concentration and extrapolating to zero concentration, they obtained 0.128 for the true equilibrium constant of the above reaction.

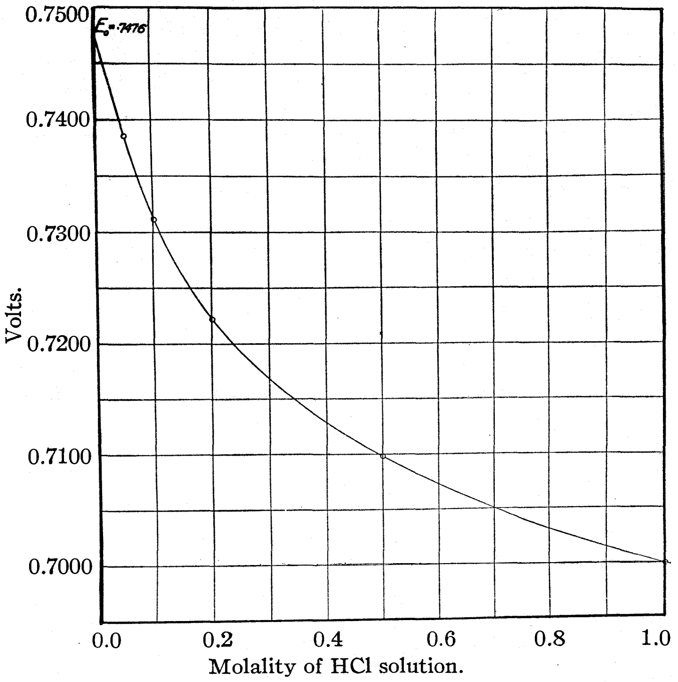


Fig. 3.—The oxidation–reduction potentials plotted against the acid concentrations.

Using −0.7995 for the potential of the silver electrode and the foregoing equilibrium constant, the normal oxidation–reduction potential of the ferric–ferrous electrode was calculated as −0.7467.

At the same time they determined the potential of the ferric–ferrous electrode to be −0.738 volt by direct e.m.f. measurements and a similar plotting of results. In the latter case, however, a salt bridge of saturated potassium chloride solution was used to eliminate liquid junction potentials. According to Lewis and Randall,[11] it is now certain that this method by no means eliminates and sometimes may even increase the

---

[10] Noyes and Brann, THIS JOURNAL, 34, 1016 (1912).

[11] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 399,

liquid potential. In view of this Lewis and Randall accept their equilibrium data as the more precise determination of the normal electrode potential. This value (—0.7467) compares quite favorably with the value determined in this study (—0.7477). Being cognizant of the errors of extrapolation we are inclined to believe that the final value of —0.7477 is uncertain by 0.5 mv.

4. The Normal Oxidation–Reduction Potential Calculated from the Principle of Total Ionic Strength.—The total ionic strengths (one-half of the sum of the molalities of each ion times the square of its valence) of the solutions used in cells of Series I were calculated. Cells E and F have a total ionic strength of less than one-tenth at which the principle of ionic strength might be expected to hold. Therefore E_0 was calculated from these cells by Equation 4. The activity coefficients of the ferrous iron were interpolated from the values given by Lewis and Randall[12] for any bivalent ion. The ferric ion activity coefficients are similarly obtained from the values given for lanthanum. The values of E_0 calculated in this manner are given in Table X.

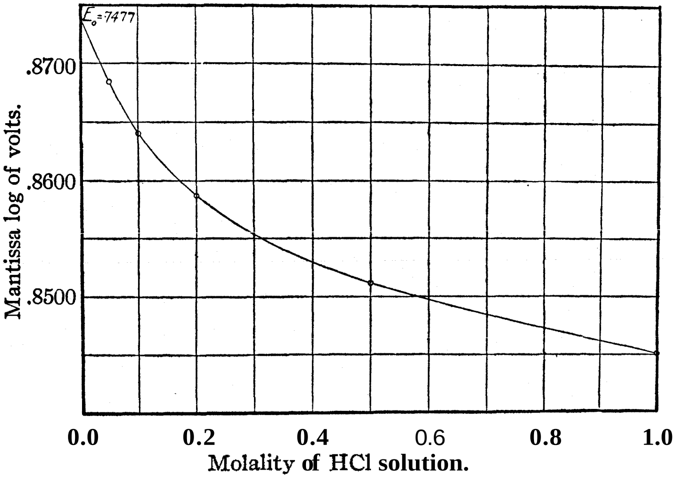


Fig. 4.—The mantissa of log of oxidation–reduction potentials plotted against the acid concentrations.

TABLE X

E_0 CALCULATED FROM IONIC STRENGTH

Cell	E	F
Total ionic strength	0.097956	0.073998
E_0	−0.7487	−0.7497

In view of the admitted uncertainties in the values for the activity

---

[12] See ref. 11, p. 382.

coefficients used the agreement with the value obtained by extrapolation in this study (−0.7477) is as good as may be expected.

In the calculation of E_0 from ionic strength the liquid junction potential was not considered. The latter was not considered because an uncertainty of one in the second decimal place of the activity coefficient of iron causes a variation of 1.3 mv. in the value of E_0.

Influence of Variation of Concentration of Iron and Acid.—The effect of decreasing the concentration of iron and acid is to increase the oxidation–reduction potentials. This is to be expected when one considers that ferric chloride forms complex salts with hydrochloric acid while ferrous chloride does not, and that the activity coefficients of a trivalent ion must increase much faster with dilution than those of a divalent ion since both become equal to one at infinite dilution. It is not safe therefore to assume, as some[13] have, that the activity coefficients of ferric and ferrous chlorides are the same.

The decrease of the oxidation–reduction potential (not the normal) with increase of the concentration of acid is in agreement with Carter and Clews[14] findings and tends to throw light (at least on half of the story) on the fact that ferrous chloride is oxidized by sulfur dioxide in strong acid solution but that ferric chloride is reduced by sulfur dioxide in dilute acid solution.

Use of Salts without Recrystallization.—It is reasonable to suppose that in the present study the salts employed need not necessarily be of "atomic weight" purity since in the extrapolations the effect of impurities will also be extrapolated to zero. J. T. Baker's best grades of ferrous and ferric chlorides were employed in one molal hydrochloric acid. The potentials coincided very closely with those obtained with the recrystallized salts. In the dilute solution the values practically coincided.

Summary and Conclusions

1. A method has been devised for the precise determination of oxidation–reduction potentials, consisting of the use of a special electrode vessel, suitable procedure, and mathematical and graphical treatment which eliminate uncertainties in former methods regarding liquid junction potentials and the activity of one electrolyte in the presence of others.

2. Methods of analysis which lead to greater precision in the determination of iron are given. A method was chosen for each analysis which gave results within 0.1% of those obtained by a widely different method. The errors of analysis were smaller than the corresponding errors in the electromotive force measurements.

---

[13] Peters, *Z. physik. Chem.*, **26**, 193 (1895). Getman, "Outlines of Theoretical Chemistry," John Wiley and Sons, New York, 1927, p. 581.

[14] Carter and Clews, *J. Chem. Soc.*, **125**, 1880 (1924).

3. The treatment with nitric acid of hydrogen electrodes which had been plated in solutions containing lead was found to be unnecessary. Thinly platinized electrodes give practically the same potentials as thickly coated ones.

4. The oxidation–reduction potentials of the ferric–ferrous electrode have been determined at various acid concentrations. It is to be emphasized that these values are of practical importance in attempting to make predictions.

5. The normal oxidation–reduction potential determined in this study compares favorably with the potential calculated from equilibrium measurements by Noyes and Brann.

6. The principle of ionic strength was applied to the calculation of the normal potential employing data obtained in 0.05 molal hydrochloric acid. The values thus calculated are in fair agreement (considering the uncertainty of activity coefficients now available) with that derived by extrapolation.

7. The value for the normal oxidation–reduction potential of the ferric–ferrous electrode determined in this study is −0.7477. The uncertainty is probably of the order of ±0.5 mv.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE PHYSIOLOGICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF MINNESOTA AND THE SOUTH CAROLINA FOOD RESEARCH COMMISSION LABORATORY IN AFFILIATION WITH THE MEDICAL COLLEGE OF THE STATE OF SOUTH CAROLINA]

THE DETERMINATION OF TRACES OF IODINE. II. IODINE IN VEGETABLES[1]

BY J. F. McCLENDON AND ROE E. REMINGTON[2]

RECEIVED SEPTEMBER 13, 1928 PUBLISHED FEBRUARY 5, 1929

In the first paper of this series[3] the general principles of a method for the determination of traces of iodine were outlined. The statement was made that an apparatus for feeding in milk powder was used. This apparatus is also useful for vegetables and consists of a steel tube with water-cooled open end and piston in the other end which is advanced by means of a screw similar to the piston of an "Alemite gun." Vegetables are made into a stick, placed in the steel tube, and advanced slowly by means of the screw and thus fed into a silica tube furnace and burned in oxygen.

---

[1] This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council of Pharmacy and Chemistry, American Medical Association.

[2] With the technical assistance of F. B. Culp.

[3] McClendon, THIS JOURNAL, 50, 1093 (1928).

Original Procedure

An outline of the apparatus is given in Fig. 1. The steel tube is of 24 mm. bore and 50 cm. long. The walls are 1 mm. thick and the threads on the screw are 2 mm. apart (pitch). Around the open end is coiled 10 turns of lead pipe, 3 mm. bore for cooling-water. The steel tube is clamped rigidly in a horizontal position. Its open end is applied to the open end of a horizontal silica tube of 36 mm. bore and 60 cm. long with an elbow extending downward of the same bore and 30 cm. long.

The horizontal portion of the silica tube is heated by five large Méker burners. Around the junction of the steel tube with the silica tube is a pyrex glass adapter of 38 mm. bore with a side neck admitting oxygen and allowing the oxygen to go into a small crack between the steel and silica tubes. The elbow of the silica tube extends downward into an absorption flask made of three 500-cc. pyrex globe flasks. In the absorption flask is placed 0.25 g. of sodium hydroxide and enough water to extend into the middle section or second globe. Some of this solution is run into the 4 Milligan wash bottles (connected in parallel) by tilting the flask. The space between the elbow and the lip of the absorption flask is stoppered with wet asbestos. The absorption flask and Milligan wash bottles stand in a tank full of ice water. The side neck of the absorption flask passes to the Milligan wash bottles and then through a small Cottrell precipitator (described in the first paper) and to a rapid air pump (Cenco rotary No. 1400) which exhausts the air at the rate of 1.25 cu. ft. per minute and causes the oxygen to flow into the open end of the silica tube.

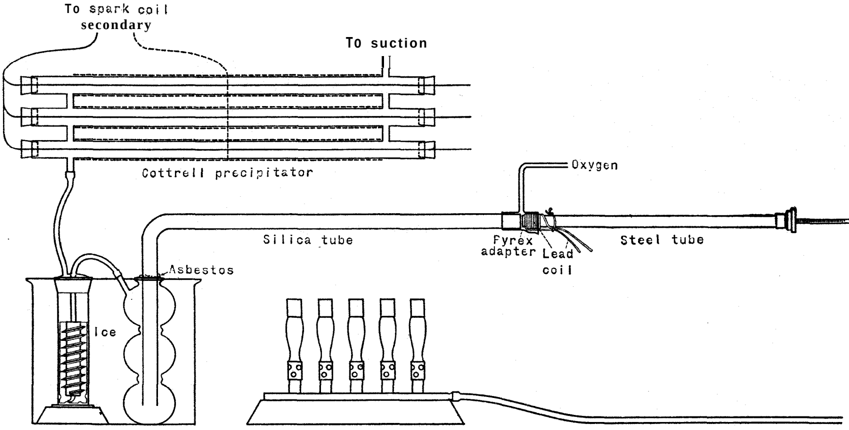


Fig. 1.

About 5 to 10 kg. of the fresh vegetables to be analyzed are ground in a suitable mill and the pulp partially dried on sheets of tin, or cheap dinner plates, in an electric oven at about 100". When the pulp reaches the consistency of putty, it is made into sticks about 50 mm. long and 24 mm. in diameter and replaced in the oven. The sticks shrink in length and diameter during further drying. In starting the combustion a stick is placed in the steel tube and the screw advanced until a few mm. of the stick extends out of the steel tube. The oxygen is turned on, the Méker burners are lighted, the pump is started and the Cottrell precipitator operated. The oxygen adapter is slid to one side and a gas flame is applied to the crack between the steel tube and the silica tube until the stick of vegetable material is ignited. The adapter is quickly replaced so that the stick burns with a white heat in oxygen. The stick is advanced by means of the screw at such a rate that it burns without the evolution of soot and tarry material. It is usually possible to advance it about 0.5 mm. per second unless it contains a great deal of fat or oil, in which case it may not be possible to advance it so rapidly. The rate of advance depends also on the rapidity of the pump, it being understood that oxygen is fed in as fast as it is sucked through by means of the pump. The ash is drawn a few cm. into the tube by the current of flue-gas. After the completion of the burning of one stick, another one is placed in the steel tube without stopping the rest of the apparatus and burned in the same way, this process continuing until the whole sample has been burned.

At the end of the combustion the contents of the large absorption flask and the wash bottle and washings of the Cottrell precipitator are evaporated in a pyrex beaker. The ash is scraped out of the silica tube and ground with the washings of the tube in *a* small ball mill using Jasper balls (from the Jasper Stone Company, Jasper, Minnesota). After grinding for several hours and until the ash is reduced to an impalpable powder, it is removed from the ball mill to a centrifuge tube or beaker, allowed to settle or centrifuged and the soluble portion transferred quantitatively by several decantations to the beaker containing the contents of the absorption flask. When the contents of the beaker have evaporated to a small volume, they are transferred to an evaporating dish, dried in an electric oven to dryness and then scraped out with a steel spatula, ground in a mortar and placed on a curved piece of sheet nickel which is placed in a pyrex combustion tube of about 30 mm. bore and 40 mm. long with an elbow which is drawn out to a much smaller bore, 20 mm. long and extends down into a side-necked test-tube. In the test-tube are placed a few milligrams of sodium hydroxide and 10 cc. of distilled water. The space between the lip of the test-tube and the elbow is plugged with wet asbestos. A suction pump is attached to the side neck. The region under the nickel boat is heated with a large, flat gas burner with the air vent opened just enough to prevent the flame from being luminous or, in other words, the pyrex tube is heated just below its softening point while air is drawn through the tube. The open end of the tube is loosely plugged with a ball of dry asbestos or glass wool so as to prevent convection currents. The heat is continued until the traces of organic matter which have escaped the first combustion are entirely burned. It is rarely necessary to redissolve the ash, filter it and burn the carbon separately. The heat of the tube should not be high enough to fuse the ash, as that will stop the combustion.

At the end of the second combustion the ash is placed in a small beaker or an evaporating dish and dissolved in the sodium hydroxide solution from the side-necked test-tube. Into it is run, drop by drop, a mixture of 90 parts of sirupy phosphoric acid and 10 parts of a solution of sulfurous acid (0.1 N or stronger and titrated recently). The addition of acid is continued until effervescence ceases. The solution is then boiled for about five minutes to expel the sulfur dioxide. It is tested with indicator paper (made by evaporating an alcoholic solution of brom phenol blue on ash-free filter paper) by removing a small drop on a glass needle and touching it to the paper. If the indicator paper does not change quickly from blue to yellow, concentrated sulfuric acid should be added drop by drop until it does change the paper as indicated.

This solution is now run into a 12-cc. separatory funnel which has an etched mark at a volume of 10 cc. and made up to the mark with distilled water. A small crystal (about 1 mg.) of sodium nitrite is added, the stopper inserted and the nitrite dissolved by agitation. One cc. of purified carbon tetrachloride (see first paper) is introduced into the separatory funnel, gently agitated or inverted 200 times so as to bring about partition-equilibrium between the iodine in the water and the carbon tetrachloride. If the carbon tetrachloride is at all cloudy, it is run into a 1 cc. centrifuge tube and centrifuged until clear. It is then placed in the left cup of a Bausch and Lomb micro-colorimeter and set at 20 mm. In the right cup of the colorimeter is placed about 1 cc.

of carbon tetrachloride containing 0.1 mg. of iodine per cc. and a color match made. An average of ten readings on the right side in mm. divided by 20 and multiplied by 0.1 (the concentration of the standard) gives the milligrams of iodine in the carbon tetrachloride, and this multiplied by 1.118 gives the milligrams of iodine in the sample analyzed. As a check on the extraction, 0.1 cc. of the water in the separatory funnel is run into a small vial containing a minute crystal of potassium iodide. A drop of carbon tetrachloride is added and the vial agitated. If the carbon tetrachloride does not become pink, a drop of conc. sulfuric acid is added to the separatory funnel and the process is repeated. If the pink color appears this time, 1 cc. of carbon tetrachloride is added to the separatory funnel, the extraction and reading are made and the yield is added to that of the first extraction.

At the end of the combustion it will be found that some ash has adhered to the silica. This is only enough to cause a slight error in the analysis but is sufficient to shorten the life of the silica tube, due to the difference in expansion of silica and ash. The life of the tube may be prolonged by rubbing off as much of the ash as possible with sand paper and then dissolving the remainder first with hydrochloric and then with hydrofluoric acid before heating the tube again. If the tube cracks off at the end it may be cut off or used for burning oils (to be described in the third paper). An elbow made by bending the silica tube is much less liable to break than an elbow that is fused on. Hence the larger tubes described in the first paper are not economical.

If the vegetables contain much chloride the wires in the Cottrell precipitator must be sealed in glass tubes run through the rubber stoppers in order to preserve the insulation.

The percentage of the total iodine caught by the Cottrell precipitator varies with the nature of the vegetable that is burned. If this percentage is determined for one sample of vegetable and found to be low it may be desirable to omit the Cottrell precipitator in analyzing similar samples, its place being taken by 4 or more Milligan wash bottles connected in parallel and a tube of 25 mm. bore 500 mm. long packed with moist glass wool. If no soot is formed the smoke is largely alkali chlorides.

In the second combustion (in the pyrex combustion tube) the material is alkaline and only a small percentage of iodine is volatilized and caught in the side-necked test-tube. This method of combustion is almost as convenient as combustion in an open crucible, however, and since some form of furnace is necessary to prevent overheating of the crucible, the pyrex tube forms a convenient type of furnace as regards visibility. If the ash fuses it may be necessary to add potassium nitrate to it for complete combustion, in which case the liability of loss of iodine from an open crucible is increased.

Some chemists have had difficulty with the method due to the material to be burned adhering to the open end of the steel tube. This is due to the tube becoming too hot or the material being in powdered form. The steel tube should not be inserted *inside* of a silica tube in which the combustion takes place. If the material is not made into sticks it may be burned in a sheet iron "boat" about 6 inches long with a handle or empty portion 18 inches long. About 30 g. of the ground vegetable or vegetable compressed into tablets is spread over the bottom of the boat, ignited and burned. The boat is withdrawn and another 30 g. added and the. process repeated until the whole is burned. Since a similar method was described in the first paper, no special details are added here except to suggest that the silica tube herein described is more economical than the larger one described in the first paper. In using the boat an oxygen inlet tube may be held up by an independent support and inserted into the silica tube as far as the most advanced end of the boat so that combustion begins at this end first and only gradually spreads over the material in the boat. The use of the boat is very unsatisfactory if the vegetable has a high fat content.

Extraction of Ash Containing Large Quantities of Soluble Salts.—The ash is extracted repeatedly in a ball mill with 95% alcohol (recently distilled over sodium hydroxide), or enough alcohol to cover the ash is added, and allowed to stand for fifteen minutes with occasional gentle stirring with a glass rod. The alcohol is decanted through a small ashless filter, the residue being retained in the dish. A second portion of alcohol is now added, and the residue rubbed with a small porcelain pestle. The ash contains considerable alkali carbonates, which extract water from the alcohol, forming a 3-phase system and the mass is at first gummy and adheres to the pestle, but later becomes pasty, so that trituration with the alcohol becomes easy. The residue is washed with a third portion of alcohol, triturating it thoroughly, and the alcohol is passed through the same filter as before.

TABLE I

ANALYSES BY THE METHOD

Potassium iodide was added to 50 g. of iodine-free starch with the following results:

Added	0.200 mg.	Found by analysis	0.194 mg.

Iodine in Vegetables from South Carolina

	Field peas	Okra	Potatoes	Sweet potatoes	Peaches
Dry matter, %	90.6	8.9	19.7	31.0	11.1
I_2, dry basis, parts per billion	197	412	333	115	192

California Vegetables

	Asparagus	Beets	Carrots	Celery	Peas	Spinach	Tomato
I_2, dry basis, parts per billion	12.0	8.0	8.0	14.0	9.0	32.0	20.0

Alternative Method Using Low-Temperature **Ashing.**—If the sample is of cereal grain (which gives an acid ash), it should be moistened with 50 cc. of 2% calcium lactate solution followed by 50 cc. of 2% sodium carbonate solution. The sample is dried, coarsely ground and heated in an evaporating dish over a small flame until the vegetable matter begins to smolder. The heat is now withdrawn so that the sample will continue to smolder and burn at low temperature, without flame. If smoldering ceases the dish may be heated again until ignited.

After this preliminary ignition, during which the sample will be completely converted into a black char, the dish is placed in a muffle and maintained at a temperature which must not exceed 450° until ashing is practically complete and the ash is light gray in color. It is not usually practicable to carry the ignition to complete whiteness of ash. This ignition in the muffle will require from twelve to fifteen hours.

TABLE II

ANALYSES BY THE LOW-TEMPERATURE METHOD

Sodium iodide was added to half of a sample of dried, ground potatoes and not to the other half and the halves were analyzed separately, with the following results:

Dry sample	Iodine, mg.
100 g. of potatoes—0.1 mg. of iodine	0.129
100 g. of potatoes	.034
Added iodine recovered	0.095 = 95%

South Carolina potatoes	Sample 1	Sample 2	Sample 3
I_2, parts per billion	338	348	369

Summary

A method has been described for the rapid combustion of vegetables for iodine analysis which necessitates the use of oxygen and special stoking to prevent soot and tar formation and results in volatilization of chlorides and iodides. These are not all caught by ordinary wash bottles. A simple form of Cottrell precipitator will precipitate all the smoke (largely alkali chlorides) provided it is large enough for the rest of the apparatus. The precipitator and mechanical stoking apparatus are shown in Fig. 1.

Low-temperature burning in open dishes requires about fifteen hours for 100-g. dry samples and does not result in large losses of iodides if the ash is alkaline and temperature never above 450°. Combustion is never complete if the ash fuses. Calcium lactate must be added to vegetables with an acid ash (cereals) in order to make the ash alkaline and prevent fusion of the ash.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF COPPER FROM THE LAKE SUPERIOR REGION AND FROM CHILE[1]

BY THEODORE W. RICHARDS AND ARTHUR W. PHILLIPS

RECEIVED SEPTEMBER 18, 1928 PUBLISHED FEBRUARY 6, 1929

Examination of the atomic weights of elements from different geographical and geological sources is of importance because of the bearing on the genesis of the elements. None of the comparisons,[2] except for products of radioactive disintegration and possibly boron, has shown any segregation of isotopes. The results here presented confirm this conclusion for the case of copper. Furthermore, they contribute to the determination of the atomic weight of this element by the analysis of yet another compound. Most of the work on the atomic weight of copper for thirty years was from the point of view of the electrochemical equivalent, which Clarke in his excellent critical review[3] shows to be inferior to the chemical method.[4]

Copper was chosen for investigation because it could be obtained from different known geological ages and from regions widely separated, because it was known to have at least two isotopes and because its atomic

---

[1] *Note by the Editor.—This* research was completed in **1923** under the direction of Professor Theodore W. Richards but the present account of it was prepared after the death of Professor Richards, by Dr. Lawrence P. Hall.

[2] For example. Richards, *Proc. Am. Acad. Arts Sci.,* **23, 178 (1887);** Richards and Cushman, *ibid.,* **33,102 (1897);** Richards, THIS JOURNAL, **24,374 (1902);** Richards and Wells, *Carnegie Inst. Pub.,* **28, 13, 17 (1905);** Baxter and Thorvaldson, THIS JOURNAL, **33, 337 (1911);** Baxter and Hoover, *ibid..* **34, 1657 (1912);** Baxter and Grover, *ibid.,* **37, 1027 (1915);** Curie, *Compt. rend.,* **172, 1025 (1921);** Gleditsch and Samdahl, *ibid* , **174,746 (1922);** Bronsted and Hevesy, Z. *anorg. allgem. Chem.,* **124,** 22 **(1922);** Dorenfeld, THIS JOURNAL, 45, **1577 (1923);** Gleditsch, *J. chim. phys.,* **21, 456 (1924);** Harkins and Stone, *Proc. Nat. Acad. Sci.,* **11, 643 (1925);** Briscoe and Robinson, *Nature,* **117, 381 (1926);** E. Gleditsch and I. Gleditsch, J. *chim. phys.,* **24, 238 (1927).** Muzaffar [THIS JOURNAL, **45, 2009** (1923)], in *a* preliminary paper, reported apparent differences in the atomic weight of antimony, depending upon the source. However, this work has been disproved by Krishnaswami [J. *Chem. Soc.,* **2534** (1927)]. Briscoe and Robinson, J. *Chem. Soc.,* **127,696** (1925), Briscoe, Robinson and Stephenson, *ibid.,* **70** (1926), Briscoe, Robinson and Smith, *ibid.,* **282** (1927), report variations in the atomic weight of boron from different sources. For examples of similarity of elements from terrestrial and meteoric origin, see Baxter and Parsons, THIS JOURNAL, **43, 507 (1921);** Baxter and Hilton, *ibid.,* **45, 694 (1923);** Baxter and Dorcas, *ibid.,* **46,357 (1924).**

[3] F. W. Clarke, "The Constants of Nature," Part V, A Recalculation of the Atomic Weights, 4th ed., Washington, **1920,** p. **125.**

[4] Since the completion of the research here recorded, Ruer and Bode [*Z. anorg. allgem. Chem.,* **137, 101** (1924)] employed the copper oxide method and found a value **63.546,** which they have defended against the criticisms of the German Atomic Weight Commission [Ruer and Bode, *Ber.,* **58A, 852 (1925);** *ibid.,* **59B, 1698** (1926)].

weight needed confirmation. One sample was obtained from the Lake Superior region and another from the Chile ore deposits.

The former, from the Calumet and Hecla Mines, contained equal parts from the upper and lower lodes. There is reason to believe that this deposit was formed not later than the Cambrian.[5] The deposits at Chuquicamata, Chile, from which the second sample came, are said to consist of a series of lodes in granitic rock, intrusive in Jurassic strata.[6]

Methods previously used for the determination of the atomic weight of copper were based on analyses of CuO, $CuSO_4$ or $CuBr_2$, and by comparison with silver, directly as well as electrolytically. For the purpose of confirmation of the atomic weight it was deemed advisable to analyze some other compound by means primarily chemical.

Tests were conducted on both cuprous and cupric chlorides to determine their suitability for analysis in the anhydrous condition. Samples of each chloride were fused in an atmosphere of chlorine in a bottling apparatus and nitrogen was used to displace the chlorine. Both cupric and cuprous chloride yielded bluish black crystals, which were partially soluble in water, giving a blue solution and a white precipitate. Under available conditions the equilibrium between cuprous chloride, cupric chloride and chlorine did not give a suitable salt.[7]

A simpler method was adopted based upon work done with cupric bromide.[8] This method, in brief, consisted in determining the copper electrolytically and the chloride content by comparison with silver in a solution of recrystallized hydrated cupric chloride.

Purification of Materials

Water, nitric acid and sulfuric acid were carefully purified and before use all were proved to be free from chloride by nephelometric tests. All alcohol and hydrochloric acid used were carefully distilled. All other reagents were also purified before use.

Pure silver was prepared from residues of silver bromide resulting from previous atomic weight work. The bromide was reduced with pure zinc, the resulting silver being washed with sulfuric acid and water before solution in nitric acid. After three crystallizations of the nitrate the silver was reduced with freshly prepared ammonium formate. The silver was thoroughly washed, fused into buttons and electrolyzed, and the crystals were again fused on lime in a hydrogen atmosphere. The resulting buttons were etched with nitric acid, washed twenty times and dried in a vacuum

---

[5] Cf. Lindgren, "Mineral Deposits," McGraw-Hill Book Co., New York, 1928, p. 509.

[6] Ref. 5, p. 958.

[7] Rose [Pogg. Ann., 38, 121 (1836)] had noticed that when cupric chloride is heated free chlorine is found in the vapors and cuprous chloride results.

[8] Richards, *Proc. Amer. Acad. Arts Sci.*, 25,195 *(1890).*

at 400°. A few of the buttons were electrolyzed again to provide small crystals used in adjusting weights of silver required in analysis. The silver was kept in a desiccator over fused potassium hydroxide.

Purification of cupric chloride was accomplished by repeated crystallization as $CuCl_2 \cdot 2H_2O$. The copper from Calumet and Hecla, Sample A, was a block of pure copper weighing about 1500 g. The center of this block was turned out on a lathe. For the first series of crystallizations 500 g. of shavings was taken; for the second series (A II) 300 g. A third series (A III) was obtained by recrystallization of the mother liquor from the first two series.

The copper turnings, washed with alcohol to remove grease, were dissolved in hydrochloric acid to which had been added a small amount of nitric acid. The cupric chloride was recrystallized four times in pyrex dishes with evaporation over the steam-bath and with centrifugal drainage. Any insoluble matter was removed by filtration after the first crystallization. Tests for iron were negative after the first crystallization. Two more crystallizations of the cupric chloride were performed in quartz dishes, evaporation in these cases taking place in vacuum desiccators over sulfuric acid. The solution was filtered after the fifth crystallization. Care was taken not to reach a high vacuum which would cause bumping and splashing. As an emergency precaution to prevent formation of hydrogen chloride by splashing solution into the concentrated sulfuric acid, watch glasses were placed beneath the quartz dishes. Since usually the crystals, forming on the surface, made a crust, the desiccator was opened from time to time and the crystals were pushed down with a glass rake. In this way was avoided the appearance of any brownish color due to the presence of anhydrous cupric chloride.

At each stage of crystallization tests were made for free hydrochloric acid. Such tests were at the best comparative. However, since each sample was purified until the same acidity was reached, the atomic weights of the different samples should be entirely comparable.

The method used in these tests was similar to that used in the analysis of cupric bromide.[8] One cubic centimeter of a concentrated cupric chloride solution was diluted to 10 cc. and one drop of methyl orange solution was added. The resulting color was purple if the solution was acidic and yellowish-green if basic. The turning point in color was marked. In order to obtain a standard for comparison the change in acidity was carefully followed in a series of nine crystallizations. These experiments showed that during the first three crystallizations all excess acid was eliminated. During the next five crystallizations the shade of purple was almost constant. The standard chosen was the purple thus produced. After the ninth crystallization the turn in color was observed. The standard purple color was restored by the addition of less than four milligrams of hydrochloric acid to a solution containing 60 g. of cupric chloride. In the crystallization of Sample A there was a slight loss of color during the first three crystallizations, but during the next three the color remained practically constant.

The Chile copper, Sample B, was received in the form of small ingots of about 200 g. each. An ingot and a half were taken for the first series of crystallizations (B I and B II). The same method of purification was followed for Sample B as for Sample A except that three crystallizations over sulfuric acid were necessary to give the normal acid test. A second set of crystallizations was performed with the mother liquors from the last four crystallizations of the first series (B III).

Analysis of Solutions

About 40 **g.** of the cupric chloride crystals was dissolved in 1100 cc. of best water in a "Non-Sol" bottle. Samples of 100 cc. each were withdrawn with a pipet using a suction pump and these samples were placed in weighed Florence flasks, which were provided with stoppers consisting of short sections of glass tubing, fitting into the neck of the flasks and supported by a small section of rubber tubing resting on the lip of the flask. The solutions were then weighed to one milligram. In half the samples the copper content was determined and in the other half the chlorine was precipitated with silver. In certain cases it was found necessary to apply a correction for the formation of atacamite. This correction will be discussed below in detail.

Determination of Copper.—The weighed sample was carefully transferred from the flask to a quartz evaporating dish and the flask rinsed many times. The solution was then evaporated on the steam-bath to dryness. The residue was taken up in a small amount of water and sulfuric acid added to convert the chloride to sulfate. The solution was again evaporated, treated with water, and evaporated to make certain of expelling all of the hydrochloric acid. The copper sulfate was dissolved in 10 *cc.* of water and transferred to a scrupulously clean, weighed platinum crucible. The evaporating dish was washed repeatedly with small portions of water and the washings were stirred into the main solution. The crucible was then made the cathode in an electrolytic stand. All the usual precautions were taken in the electrolysis. The washings were collected and tested for copper. The crucible was dried at 85° before the first weighing and at 120° before reweighing. In every analysis the deposit of copper was smooth, firm, even, coherent and of bright, uniform color. No flakes and no crystalline character were observed.

The washings were evaporated to about 10 cc., made alkaline with ammonium hydroxide, evaporated and heated gently to drive off ammonium sulfate. The residue was taken up in 5 cc. of water and tested for copper with potassium ferrocyanide. In every case a faint coloration resulted, The amount of copper which would cause this coloration was ascertained by comparison with known amounts of copper. The amount of undeposited copper was quite uniform in the washings from different analyses and amounted to 0.00006 g. This correction was applied to all analyses.

Determination of Chlorine.—A weighed sample of cupric chloride solution was transferred to a 3-liter precipitation flask. With fifteen or more rinsings of the Florence flask the solution was diluted to 500 cc. From the previous copper determination the equivalent amount of silver was calculated (assuming 63.565 as the atomic weight of copper) and weighed out with proper allowance for weight corrections and for the buoyancy of air. The silver was dissolved in nitric acid in a flask with a bulb tower and the resulting solution diluted to 500 cc. The silver solution was then added to the cupric chloride solution in a dark room, in which all further work with the solution was conducted. By the usual nephelometric tests over a period of several months the exact end-point was measured.

Correction for Atacamite

After solution **A I** had stood for a few days a slight precipitate was observed at the bottom of the container. Upon examination this precipitate was found to consist of small clusters of fine, light-green rhombic crystals which had grown from the solution. Their form and color indicated that they might be cupric oxychloride or atacamite, sometimes written $CuCl_2{\cdot}3CuO{\cdot}4H_2O$. In the early work on cupric bromide a similar precipitate had been found and made the subject of a short paper.[9]

Solution A I was filtered and kept for six months. No further growth of crystals was observed. The second solution A II was carefully watched. Seven days after the recrystallized cupric chloride had been dissolved crystals were observed. This solution was left for four months before being filtered. The crystals were then analyzed and the solution was used for atomic weight determinations. In the meantime solution A III was prepared, but with the addition of one cubic centimeter of nitric acid (40%) to a concentrated solution of the crystals before dilution. As no crystals grew in solution A III in forty days, the solution was analyzed.

Solution B I yielded crystals in five days. After fifteen days the crystals were collected on a Gooch-Munroe crucible. This solution stood for four months without any more crystals appearing. Solution B II was prepared from the same crystals as solution B I. However, in this case one cubic centimeter of nitric acid was added to the first concentrated solution before final dilution. In the case of solution B III crystals were found on

---

[9] Richards, *Proc. Am. Acad. Arts Sci.*, *25*, *215 (1890)*.

the fourth day. This solution was filtered after twenty-one days, the crystals were investigated and the solution was analyzed.

Apparently the growth of crystals was complete in a week. It is significant that the weights of the crystals were practically the same in solutions B III and A II.

The precipitates from these two solutions were washed with distilled water and dried at 120° to constant weight. They were then dissolved in nitric acid and the chlorine was determined as silver chloride. Excess silver was removed with hydrobromic acid, and after conversion to the sulfate the copper was determined electrolytically. The results of the analyses are given in Table I.

TABLE I

ANALYSIS OF PRECIPITATES

Soln.	Precipitate, g.	AgCl, g.	Chlorine, g.	Copper, g.	Copper, %	Chlorine, %
A II	0.02262	0.01572	0.00389	0.01294	57.2	17.2
B III	.02277	.01540	.00381	.01305	57.3	16.7

The copper content of atacamite should be 57% according to the formula usually assigned it. The chlorine content was likewise slightly higher than theoretical, but since the ratio of chlorine to copper was similar to that for atacamite, it was concluded that the crystals consisted of this compound,

It was necessary to investigate the method of formation of this precipitate, because in it the weight of chlorine was much smaller on the basis of the copper present than in pure cupric chloride. If this difference of chlorine had'been retained in solution in the formation of the atacamite, there would be an excess of chlorine in the solutions from which the precipitate had been removed. On the other hand, if in some way the chlorine had escaped from solution, no correction for excess chlorine would be necessary in the case of removal of the precipitate. But in the cases where the atacamite was held in solution with nitric acid, a loss of chlorine would mean an excess of copper or a deficiency of chlorine, and a correction need be added to the chlorine found in the analysis of the solution. For example, in the atacamite from solution A II the weight of chlorine found was 0.00389 g., whereas the weight of chlorine required for an equivalent amount of $CuCl_2$ is 0.01443 g. This difference of 0.01054 g. of chlorine corresponds in the chloride analysis to 0.03207 g. of silver for the whole solution or 0.00291 g. of silver for each 100-cc. sample analyzed. Similarly for solution B III the difference in silver would be 0.00297 g. for each 100-cc. sample.

It became important then, to find out whether the chlorine left the solution or not. This problem was attacked in several ways. The acidity of the solutions was carefully followed before and after precipitation of the oxychloride. Since acidity was no greater after precipitation of atacamite than before, it appeared that the atacamite was not formed by hydrolysis.

If cuprous chloride had been present in the crystals of cupric chloride, oxidation of the cuprous chloride to cupric would have formed the oxychloride.[10] Both cuprous chloride and atacamite are soluble in concentrated cupric chloride. Growth of crystals from solution would require some time. On this conjecture, to test for loss of chlorine, a solution of purest cupric chloride was placed in a vacuum desiccator for evaporation over chloride-free sulfuric acid. Ten cubic centimeters of saturated potassium hydroxide solution was placed within the desiccator. After one month the potassium hydroxide was tested. Compared with a blank test with a similar unexposed solution of potassium hydroxide, an increase in chloride content of the hydroxide was found.

A second test was conducted in a similar manner except that the cupric chloride solution was treated with a little potassium hydroxide. This solution could not have contained excess acid or chlorine. Again the potassium hydroxide gained chlorine.

In order to determine whether this loss during crystallization was chlorine or hydrochloric acid, pure cupric chloride crystals, moistened with water, were placed in a desiccator over chloride-free sulfuric acid with all the precautions previously employed. A strip of starch-iodide paper was suspended within the desiccator. Although the strip was moistened when introduced it quickly became dry. In two months the paper was distinctly purple, whereas in a blank test the paper did not change in color.

Since this test with dry starch-iodide paper was not entirely convincing, a more delicate method was tried. In accordance with a method proposed by Ganassini[11] a strip of chlorine-free filter paper was moistened with a 10% solution of potassium bromide, dried, then dipped into a 0.04% ammoniacal alcoholic solution of fluorescein and again dried. When this paper was left in a vacuum desiccator with moist cupric chloride crystals, it gradually became pink, due to conversion of fluorescein into eosin. The first coloration was observed in seven days. The color developed for about one month, after which no increase in intensity was observed. Blank tests with fluorescein-bromide paper showed no change in color.

It appeared, then, that chlorine was lost in the crystallization of the cupric chloride, undoubtedly from formation of cuprous chloride. The atacamite resulted, not from hydrolysis, but most probably from oxidation of cuprous chloride and crystallization of this rather insoluble complex on dilution and long standing. It seems probable from Henry's Law that all of the free chlorine left the solution. The chlorine lost was undoubtedly represented by the precipitate on account of the insolubility of the atacamite. Agreement of analyses with and without atacamite in

---

[10] Cf. Gröger, *Z. anorg. Chem.*, **28, 154 (1901).**

[11] Ganassini, ***Chem. Zentr.*, I, 1172 (1904).**

the solution further corroborates the hypothesis. The experience with cupric chloride is quite comparable with that with the bromide.[12]

In the analyses, therefore, a correction was added of silver equivalent to the chlorine lost in the cases of solutions A III and B II where the precipitate was dissolved in nitric acid. The correction was based upon the analysis of atacamite from the other solutions and could be legitimately applied because of the similarity of treatment accorded the different series of crystallizations, because all samples gave identical tests for acidity and because the weights of precipitates in the other solution were similar, No correction was applied for solutions A II and B III where the precipitate was removed from the solution.

In Tables II to V are recorded the results of all the successful analyses with the exception of several preliminary ones performed only for practice. Solutions A I and B I were used in the investigation of atacamite.

All values given have been corrected to vacuum. In calculating the necessary corrections the following densities were used: weights, 8.4; $CuCl_2$ solutions, 1.02; silver, 10.49. The atomic weight of copper is referred through chlorine directly to the atomic weight of silver, which was taken as 107.880.

The atomic weights of the samples of copper from Calumet and Hecla and from Chile are identical within the limit of accuracy of the present methods. Neither the correction for atacamite nor the question of acidity influences this comparison. It is a striking case of identity of isotopic constitution of a chemical element taken from sources differing greatly in geological age and geographical distribution.

TABLE II

ANALYSIS OF CUPRIC CHLORIDE FROM LAKE SUPERIOR COPPER (SOLUTION A II)

Copper Analyses

Sample	Corr. wt. of sample, g.	Corr. wt. of copper found, g.	Copper correction	Corr. copper per 100 g. of soln., g.
4	101.833	1.20672	+0.00006	1.18505
5	101.821	1.20660	+ .00006	1.18508
6	101.879	1.20730	+ .00006	1.18509
			Average	1.18507

Chlorine Analyses

Sample	Corr. wt. of sample, g.	Corr. silver weighed out, g.	Nephelometer correction	Corr. silver equiv. for sample, g.	Corr. silver equiv. per 100 g. of soln., g.
1	101.740	4.09307	+0.00010	4.09317	4.02317
2	101.836	4.09737	− .00079	4.09658	4.02272
3	101.788	4.09475	+ .00026	4.09501	4.02308
				Average	4.02299

From 4.02299 : 1.18507 = 215.760 : X, $X = 63.557$, **the atomic weight of copper.**

---

[12] **Ref.** 8, **p.** 200.

TABLE III

ANALYSIS OF CUPRIC CHLORIDE FROM LAKE SUPERIOR COPPER (SOLUTION A III)

Copper Analyses

Sample	Corr. wt. of sample, g.	Corr. wt. of copper found, g.	Copper correction	Corr. copper per 100 g. of soln., g.
6	102.333	1.29116	+0.00006	1.26182
7	102.279	1.29064	+ .00006	1.26194
8	102.408	1.29229	+ .00006	1.26196
9	102.424	1.29239	+ .00006	1.26186
10	102.462	1.29298	+ .00006	1.26197
			Average	1.26191

Chlorine Analyses

Sample	Corr. wt. of sample, g.	Corr. silver weighed out, g.	Nephelometer correction	Corr. for loss of chlorine	Corr. silver equiv. for sample, g.	Corr. silver equiv. per 100 g. of soln, g.
1	102.533	4.39201	−0.00282	+0.00291	4.39210	4.28360
2	102.399	4.38642	− .00255	+ .00291	4.38678	4.28400
3	102.411	4.38689	− .00248	+ .00291	4.38732	4.28400
4	102.351	4.38441	− .00262	+ .00291	4.38470	4.28395
5	102.338	4.38386	− .00272	+ .00291	4.38405	4.28390
					Average	4.28389

From 4.28389:1.26191 = 215.760:X, X = 63.557, the atomic weight of copper.

TABLE IV

ANALYSIS OF CUPRIC CHLORIDE FROM CHILE COPPER (SOLUTION B II)

Copper Analyses

Sample	Corr. wt. of sample, g.	Corr. wt. of copper found, g.	Copper correction	Corr. copper per 100 g. of soln., g.
6	102.355	1.28032	+0.00006	1.25092
7	102.398	1.28075	+ .00006	1.25082
8	102.370	1.28045	+ .00006	1.25087
9	102.366	1.28041	+ .00006	1.25088
10	102.357	1.28030	+ .00006	1.25088
			Average	1.25088

Chlorine Analyses

Sample	Corr. of sample, g.	Corr. silver weighed out, g.	Nephelometer correction	Corr. for loss of chlorine	Corr. silver equiv. for sample, g.	Corr. silver equiv. per 100 g. of soln., g.
1	102.308	4.34115	+0.00054	+0.00291	4.34460	4.24660
2	102.295	4.34085	+ .00007	+ .00291	4.34383	4.24637
3	102.370	4.34399	+ .00005	+ .00291	4.34695	4.24621
					Average	4.24639

From 4.24639:1.25088 = 215.760:X, X = 63.557 the atomic weight of copper.

TABLE V

ANALYSIS OF CUPRIC CHLORIDE FROM CHILE COPPER (SOLUTION B III)

Copper Analyses

Sample	Corr. wt. of sample, g	Corr. wt. of copper found, *g*.	Copper correction	Corr. copper per 100 g. of soln., g.
4	101.881	1.28720	+0.00006	1.26350
5	101.941	1.28794	+ .00006	1.26348
6	101.927	1.28748	+ .00006	[1.26321]*
			Average	1.26349

Chlorine Analyses

Sample	Corr. wt. of sample, g.	Corr. silver weighed out, g.	Nephelometer correction	Corr. silver equiv. for sample, g.	Corr. silver equiv. per 100 g. of soln., *g*.
1	101.897	4.37043	+0.00021	4.37064	4.28926
2	101.974	4.37377	− .00005	4.37372	4.28905
3	101.929	4.37153	+ .00052	4.37205	4.28931
				Average	4.28921

From 4.28921:1.26349 = 215.760:X, X = 63.557, the atomic weight of copper.

*Since the third copper analysis is widely divergent from the other two it is omitted in computing the average. If included the atomic weight of copper found from solution B III becomes 63.554.

The value found by the analysis of cupric chloride adds valuable evidence to the atomic weight of copper. The condensed results of **all** accepted analyses are listed in Table VI.

As a result of fifteen copper determinations and fourteen chlorine determinations the atomic weight of copper is found to be **63.557.**

This value does not seem to be influenced perceptibly by the formation of atacamite, since identical values are obtained whether the atacamite is removed or dissolved and due allowance made for it. The relative acidity, while not affecting the comparison of the samples, since all gave the same indicator test, might have caused a slight deviation from **a** true value. From experimental evidence the total change from a distinctly acidic to a distinctly basic reaction would correspond to **0.006** unit in atomic weight. If it is assumed that the true acidity for the cupric chloride solutions was midway between these conditions, the atomic weight found would be about **0.003** unit low.

TABLE VI

ATOMIC WEIGHT OF COPPER

From solution A II	63.557
From solution A III	63.557
From solution B II	63.557
From solution B III	63.557
Grand average	63.557

Acknowledgment for generous financial assistance in this research is made to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory.

Summary

No difference was found in the atomic weights of specimens of copper from the Calumet and Hecla mines in the Lake Superior region in Michigan and from Chuquicamata, Chile.

The ratio of the atomic weight of copper to that of silver was determined by analysis of pure, recrystallized cupric chloride. The copper was determined electrolytically and the chlorine by nephelometric titration with pure silver. On the basis of Ag = 107.880 the atomic weight of copper was found to be **63.557.**

CAMBRIDGE, MASSACHUSETTS

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

THE SURFACE TENSION OF LIQUID SULFUR DIOXIDE

BY VERNON M. STOWE

RECEIVED OCTOBER 1, 1928 PUBLISHED FEBRUARY 5, 1929

The surface tension of liquid sulfur dioxide has been determined once only and that at a single temperature. At −25° Grunmach[1] found the surface tension of the liquid to be **33.5** dynes per cm. The author has been interested for several years in the work of Dr. Bond[2] of the University of Iowa on solubility. Now Hildebrand[3] recounts the relation between surface tension and solubility. Therefore, it seemed very desirable to determine the surface tension of liquid sulfur dioxide at several temperatures in order that comparisons might be made with other liquids. The problem of the solubility relations of liquid carbon dioxide has already been attacked in this same manner by Quinn.[4]

Experimental

The capillary tube method was used. **A** large number of capillary tubes were drawn from a variety of soft glass tubes and of these six were chosen for uniformity of bore, determined by means of a micrometer. They were washed with a mixture of potassium dichromate and sulfuric acid for over twenty-four hours. They were thoroughly rinsed with tap water, then with distilled water and finally with conductivity water. They were dried by drawing air through them briefly and were placed in a desiccator over phosphorus pentoxide for more than a week. From the time they were removed from the cleaning solution they were handled with carefully cleaned hands and only at one end. This end was broken off immediately to prevent impurities from

---

[1] Grunmach, *Ann. Physik,* [4] 4, 367 (1901).

[2] Bond and Beach, THIS JOURNAL, **48,** 348–356 (1926); various University of Iowa theses.

[3] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924.

[4] Quinn, THIS JOURNAL, 49,2704 (1927).

spreading down onto the cleaned portion. The capillaries were loaded into tubes of heavy pyrex glass **1.35** cm. in diameter, sealed at one end. These tubes had been thoroughly cleaned and dried in the same manner as the capillaries. The capillaries were held in a position along the axis of the "jacket" tube by means of two platinum wires bent into a bracket shape, with a loop in the middle. The upper part of the jacket tube **was** constricted to make subsequent sealing easy.

Liquid sulfur dioxide was prepared by the method mentioned by Bond and Beach" except that no mercury seal was used. The apparatus was well swept out by preparing several portions of the liquid. It boiled at −9.8° at 736 mm. pressure, leaving no residue. The jackets were filled about one-fourth full and sealed off at a length of about **10** cm.

A thermostat was constructed of a quart size unsilvered wide-mouthed Dewar flask. This was cooled to **−90** and −50° by pouring liquid air into a long test-tube and inserting this tube into the thermostat liquid. Ethyl alcohol was used at the low temperatures. The slcohol would congeal about the tube and furnish a fairly even temperature for some time as it thawed. Ice and calcium chloride were used for the temperature −20°, and salt and ice for **−10** and −5°. Ice water and much ice were used for the 0° point. Water at 4° was used to cool tap water to achieve temperatures between 0 and 25°. Temperatures of **30** to 50° were attained by inserting a long narrow lamp commercially used for illuminating showcases. This was turned off and on by means of a home made thermoregulator containing toluene and a mercury contact column. The temperature could easily be controlled within one-tenth of one degree. The light was turned on and off several times per second even when all vibration was eliminated. The bath was stirred efficiently at all temperatures.

The thermometers were checked against one or two standard thermometers recently calibrated by the U. S. Bureau of Standards. At sub-zero temperatures it was necessary to check against freezing and sublimation points. Carbon dioxide, mercury, chloroform, chlorobenzene and carbon tetrachloride were used.

Tubes were kept at the required temperature for thirty minutes to one hour before readings were taken. When working at temperatures somewhat removed from room temperatures, they were placed in a crude cooling bath or warming bath in order that they might come quickly to equilibrium when used.

Readings of the height of the column in the capillary were made by means of a good heavy cathetometer. At least five readings checking within ±0.01 cm. were made. These readings were made with the tube suspended in the thermostat in at least two different positions and at different levels to eliminate errors due to distortion of light by the Dewar flask and the jacket tube. Discrepancies due to this cause were rare. The averages of these readings are recorded in Table II.

After reading the height of the liquid in the capillaries at the various temperatures the tubes were opened. When the sulfur dioxide had completely evaporated, they were rinsed out with some carbon tetrachloride which had been purified by freshly distilling in a tin–glass–air system followed by fractional crystallization. The tubes were now charged with some of the purified carbon tetrachloride, which has a surface tension very close to the value for sulfur dioxide at 20°. The tubes were now suspended in the thermostat and readings were made of the capillary rise. Assuming Richards and Carver's[5] value for the surface tension of carbon tetrachloride to be correct, the radii of the capillaries were calculated

---

[5] Richards and Carver, THIS JOURNAL, 43, **845 (1921).**

from the equation $r = 2\gamma/hdg$, where r is the radius of a capillary, h is the capillary rise corrected as shown below, d is the density of carbon tetrachloride at 20°, g is the acceleration due to gravity and γ is the surface tension of carbon tetrachloride at 20°. The values so found for the radii are listed in Table I.

A second method was employed to determine the radii. A thread of mercury was introduced into each capillary tube and the length of the thread was measured by a micrometer in conjunction with a steel decimeter scale. Incidentally, a check on the uniformity of bore of the capillaries was made by moving the thread along. The length remained practically constant in all cases. The radii were calculated in the obvious manner, after using a microbalance to weigh the mercury by difference. These values are given in the third column of Table I.

The radii were determined finally by breaking the capillaries off squarely and examining them under a microscope fitted with a micrometer. These results are listed in the fourth column of Table I. The mercury method was probably the most exact and these values are used. The fifth and sixth columns give the percentage of deviation from the mercury values. The author did not examine the probable error of these methods. The agreement between the sets was considered very satisfactory.

TABLE I

RADII OF THE CAPILLARY TUBES IN CENTIMETERS

Tube	Method 1st, CCl_4	 2d, Hg	 3d, ocular	Deviations 1st, %	 3d, %
1	**0.01978**	**0.01950**	**0.01995**	+1.4	+2.3
2	.01840	.018632	.01868	+1.3	+0.3
3	.00923	.009135	.00923	+1.0	+1.1
4	.01692	.017117	.01736	−1.2	+1.4
5	.02677	.02737	.02729	−0.5	−0.3
6	.01409	.014222	.01430	−0.9	+0.6

Results

The calculations were made in the same manner as those performed by Quinn in the article mentioned. Table II lists the temperature, the tube number, the observed height, the height after two corrections had been made, the densities of the liquid and of the gas, the difference between these values, the surface tension and the average of these numbers at each temperature. The corrections were for volume of the meniscus, and a correction for the effect of the outer tube, made in the same manner as Quinn made them. The densities were read from a large graph upon which had been plotted all the data of densities listed by "International Critical Tables." They were extrapolated mechanically where necessary. Tube No. 3 was thrown out entirely because it was not properly filled with the liquid.

TABLE II

SURFACE TENSION OF SULFUR DIOXIDE

t	Tube	h_1	h_2	D	d	$D - d$	γ	Av. γ
−79	1	2.185	2.258	1.615	0	1.615	(34.07)	
−79	2	2.51	2.589				(38.19)	
−84	4	3.05	3.138				42.53	
−79	5	1.89	1.980				42.91	
−81	6	3.62	3.705				41.72	
−50	1	2.465	2.546	1.5572	0.002	1.555	37.85	
−50	2	2.04	2.106				(29.91)	
−50	4	2.76	2.840				37.06	
−50	5	1.705	1.787				37.29	
−52.3	6	3.300	3.377				36.60	
−20.3	1	2.10	2.170	1.4846	.003	1.482	30.74	
−20	2	2.22	2.291				31.00	
−19.8	4	2.35	2.419				30.08	
−20.2	5	1.48	1.553				30.88	
−20.3	6	2.90	2.969				30.68	30.68
−10	1	1.965	2.031	1.4601	.003	1.457	28.29	
−10	2	2.10	2.167				28.84	
−10	4	2.27	2.337				28.57	
−10	5	1.405	1.474				28.82	
−10	6	2.735	2.800				28.45	28.59
− 5.4	1	1.93	1.995	1.4476	.003	1.445	27.56	
− 5.9	2	2.05	2.116				27.93	
− 5.8	4	2.20	2.265				27.46	
− 6.1	5	1.36	1.428				27.69	
− 5.8	6	2.70	2.765				27.86	27.70
+ 0.2	1	1.86	1.923	1.4350	.004	1.431	26.30	
+ 0.15	2	1.975	2.039				26.65	
+ 0.20	4	2.14	2.203				26.45	
+ 0.30	5	1.34	1.407				27.02	
+ 0.3	6	2.57	2.632				26.87	26.66
+ 5	1	1.82	1.882	1.4223	.004	1.418	25.51	
+ 5	2	1.91	1.972				25.54	
+ 5	4	2.08	2.142				25.49	
+ 5	5	1.30	1.365				25.97	
+ 5	6	2.505	2.566				25.37	25.58
+ 9.9	1	1.76	1.820	1.4095	.0045	1.4050	24.45	
9.9	2	1.87	1.931				24.78	
9.9	4	2.02	2.080				24.52	
9.9	5	1.26	1.323				24.94	
9.9	6	2.445	2.504				24.53	24.54
15	1	1.705	1.763	1.3964	.005	1.3914	23.45	
15	2	1.795	1.853				23.55	
15	4	1.96	2.019				23.58	
15	5	1.225	1.287				24.03	
15	6	2.375	2.433				23.60	23.64
20	1	1.67	1.727	1.3831	.0055	1.3776	22.75	
20	2	1.755	1.812				22.80	
20	4	1.90	1.956				22.61	

TABLE II *(Concluded)*

t	Tube	h_1	h_3	*D*	*d*	*D* − *d*	γ	Av. γ
20	5	1.18	1.240				22.92	
20	6	2.29	2.346				22.54	22.72
24.8	1	1.59	1.655	1.3695	.0060	1.3635	21.57	
24.8	2	1.70	1.756				21.87	
24.9	4	1.84	1.895				21.68	
24.9	5	1.14	1.198				21.42	
24.9	6	2.21	2.264				21.52	21.61
30	1	1.54	1.593	1.3556	.0070	1.3486	20.54	
30	2	1.63	1.684				20.75	
30	4	1.77	1.823				20.63	
30	5	1.105	1.162				21.03	
30	6	2.15	2.203				20.72	20.73
+40	1	1.44	1.490	1.3264	.0100	1.3164	18.75	
40	2	1.515	1.565				18.82	
40	4	1.65	1.70				18.78	
40	5	1.02	1.073				18.95	
40	6	1.975	2.023				18.57	18.77
50	1	1.32	1.366	1.2957	.0144	1.2813	16.73	
50	2	1.395	1.442				16.88	
50	4	1.515	1.561				16.78	
50	5	0.94	0.99				17.02	16.85

Discussion

The equation of de Block mentioned by Quinn was applied to the data between −20° and +50° and found to fit within 0.5%. This equation states that $\gamma = K(t_c - t)^n$, where t is the temperature concerned, in degrees centigrade, t_c is the critical temperature, γ is the surface tension and K $= \gamma_0/(t_c)^n$. Here γ_0 is the surface tension at 0° and n is *a* constant, equal to 1.2 for most normal unassociated liquids. In the present work n was determined for each experimental datum and the values were averaged, yielding 1.19. However, the median value seemed more desirable on inspection. This value for n is 1.20. The surface tension was therefore

TABLE III

CALCULATED RESULTS

t, °C.	n	$\gamma_{\text{obs.}}$	$\gamma_{\text{calcd.}}$ (n = 1.2)	Diff.	$\gamma_{\text{calcd.}}$ (n = 1.19)	Diff.
−20	1.17	30.68	30.70	+0.02	30.74	+0.06
−10	1.13	28.59	28.70	+ .11	28.69	+ .10
− 5.8	1.06	27.70	27.84	+ .14	27.83	+ .13
+ 5	1.28	25.58	25.65	+ .07	25.66	+ .08
+ 9.9	1.27	24.54	24.66	+ .12	24.68	+ .14
+15	1.20	23.64	23.64	0	23.67	+ .03
+20	1.20	22.72	22.65	− .07	22.68	− .04
24.5	1.22	21.61	21.69	+ .08	21.73	+ .12
30	1.19	20.73	20.69	− .04	20.73	0
40	1.20	18.77	18.76	− .01	18.81	+ .04
50	1.20	16.85	16.86	+ .01	16.92	+ .07

calculated from both equations, $y = 0.061534(157.5-t)^{1.2}$ and $\gamma = 0.06473(157.5-t)^{1.19}$. The results are entered in Table III, with the deviations of each from the experimental values. The value $n = 1.20$ appears to fit slightly better than $n = 1.19$, although the latter yields smaller maximum deviations. The critical temperature was taken from the work of Cardoso and Fiorentina.[6]

The functions mentioned by Hildebrand,[3] in which E_σ = the total energy of surface formation and v = molal volume, were evaluated as follows: $E_\sigma = 79$ at 20°; $\gamma/v^{1/3} = 6.33$ at 20°; $E_\sigma/v^{1/3} = 22$ at 20°. The second function classifies sulfur dioxide between chloroform and benzene in the Hildebrand solubility table.

Numerical values were substituted in the equation of Ramsay and Shields.[7]

$$\frac{\gamma_1\,(M/d_1)^{2/3} - \gamma_2\,(M/d_2)^{2/3}}{t_2 - t_1} = k$$

The data for -20 and $+50°$ place the value of k at 2.134. Non-polar liquids average about 2.12.

This work represents a repetition and an extension of crude experiments reported before the North Dakota Academy of Science on May 4, 1928. The author wishes to express his thanks to Dr. S. C. Lind, Director of the School of Chemistry of the University of Minnesota, for his courtesy in placing facilities of the School at his disposal.

Summary

1. Measurements of the surface tension of liquid sulfur dioxide are reported at temperatures from +50 to $-20°$ with less accurate measurements down to $-80°$ in the undercooled region.
2. The equation of de Block in the form $\gamma = 0.061534(157.5-t)^{1.2}$ is found to fit the experimental data excellently over a 70° range.
3. Several constants depending upon the value of the surface tension are calculated. Results classify liquid sulfur dioxide with benzene and chloroform in its solubility relations.

MINNEAPOLIS, MINNESOTA

---

[6] Cardoso and Fiorentino, *J. chim. phys.*, 23,841 (1926).

[7] Getman, "Outlines of Theoretical Chemistry," John Wiley and Sons, Inc., New York, 1918, p. 148.

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

THE ELECTROMOTIVE FORCES OF UNI-UNIVALENT HALIDES IN CONCENTRATED AQUEOUS SOLUTIONS

BY HERBERT S. HARNED

RECEIVED OCTOBER 5, 1928 PUBLISHED FEBRUARY 5, 1929

Measurements of flowing amalgam cells of the type

$$Ag \mid AgX \mid MX(m_2) \mid M_xHg \mid MX(m_1) \mid AgX \mid Ag$$

in which MX is an alkaline halide, have been made by a number of investigators.[1] Accurate results of this character are of fundamental importance since they measure the partial free energy of the solute relative to a given concentration directly, and thus afford a means of computing the activity coefficients. Further, these electromotive forces are of considerable use for the calculation of other quantities, as, for example, the dissociation of water in salt solutions.[2] For these reasons, a more searching, precise and thorough study than heretofore made of the cells containing potassium and sodium chlorides and bromides will be presented, as well as results of less accuracy with cells containing lithium chloride and bromide. Certain experimental difficulties which were encountered will be pointed out and the concentration range in which these measurements may be expected to be valid will be indicated.

Materials and Electrodes.—The mercury employed was distilled three or more times. All the salts were purified by recrystallization of high grade analyzed chemicals. The sodium and potassium chlorides were precipitated by hydrochloric acid gas and then fused. The recrystallized sodium and potassium bromides were dried for two days or more at a temperature of 200–250°. Solutions of these salts were made by direct weighing of both salt and water. Concentrated solutions (approximately 12 M) of lithium chloride and bromide were made from the recrystallized salts and analyzed gravimetrically. These stock solutions were diluted to the desired strength by mixing with the required weight of water.

The amalgams of potassium and sodium were made by the method described by Harned[3] and always contained approximately 0.01% of the alkali metal. Lithium amalgam of approximately 0.003% as recommended by Harned and Swindells[4] was employed. It was made by the electrolysis of a solution of the hydroxide. We have never encountered serious difficulties in the use of sodium or potassium amalgams. Lithium amalgam, however, is much more difficult to control and consequently results obtained with it are considerably less reliable than those obtained with the sodium and potassium amalgams.

Three kinds of silver-silver chloride electrodes have been employed. **Type 1.**

---

[1] (a) MacInnes and Parker, THIS JOURNAL, 37, 1445 (1915); (b) MacInnes and Beattie, *ibid.*, 42, 1117 (1920); (c) Allmand and Polack, J. Chem. *Soc.*, 115,1020 (1919); (d) Pearce and Hart, THIS JOURNAL, 43, 2483 (1921); (e) Harned and Douglas, *ibid.*, 48, 3095 (1926).

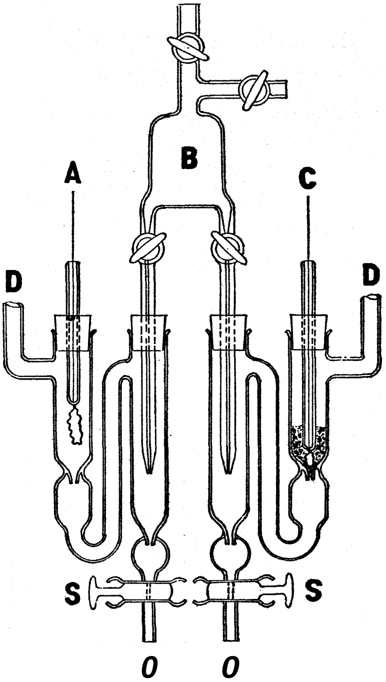
[2] Harned, *ibid.*, 47, 930 (1925).

Warned, *ibid.*, 47, 676 (1925).

[4] Harned and Swindells, *ibid.*, 48, 126 (1926).

A platinum spiral filled with a paste of silver oxide was heated to 450°. The silver electrode thus obtained was surrounded by crystalline silver chloride, obtained by the slow evaporation over sulfuric acid of an ammoniacal silver chloride solution. This type of crystalline silver chloride was recommended by Giintelberg[6] for this purpose. Type 2. A platinum spiral which held silver obtained from heating the oxide paste was made the anode in a normal hydrochloric acid solution and the chloride was formed by slow electrolysis at low current densities (20 ma. per cc. electrode for two hours). Type 3. These electrodes were the same as recommended by Noyes and Ellis,[6] and were the same as Type 2 with the exception that a layer of electrolytic silver was deposited upon the spiral by electrolysis of a potassium silver cyanide solution before the silver oxide paste was put on.

Apparatus and Methods of Measurement.—The cell finally employed (Fig. 1) was of a very simple design. It could be filled readily through the tubes DD with solutions which had been previously boiled *in vacuo*. It also could be completely emptied by suction through the outlets OO. This method of filling and emptying the apparatus has been sufficiently described elsewhere.[7] A Type 1 electrode is represented by C. A small ball of glass wool at the narrow opening in the tube was used to hold the crystalline silver chloride. Electrodes of Types 2 and 3 are represented by A. In the actual measurements, electrodes of the same type were used in each of the two cell compartments. The stopcocks SS which had to be manipulated during the course of a measurement are shown to contain grease cups at the two ends. By filling these with a rubber–vaseline–paraffin mixture, they could be manipulated under the water in the thermostat without danger of electrical leakage. The amalgam reservoirs, B, were of the design used by MacInnes and Beattie. In the cases of potassium and sodium chlorides and bromides, and lithium bromide, three amalgam reservoirs were employed. A measurement would be made with the first, then the cell emptied and refilled with the same solution. The second amalgam reservoir was then introduced and another measurement obtained. This manipulation was repeated until all three amalgam reservoirs were used. Reservoir No. 1 delivered 1 cc. of amalgam in fifteen seconds from the left capillary and 1 cc. in twenty-five seconds from the right capillary. Reservoir No. 2 delivered 1 cc. in fifteen seconds from both capillaries. Reservoir No. 3 delivered 1 cc. in twenty-five seconds from the left and the same amount from the right capillary in fifteen seconds. Two ways of forming the amalgam electrodes were employed when using potassium and sodium amalgams. One was to allow the jets of amalgam from the capillaries to break in the solution. This could be done by removing the amal-



Pig. 1.

---

[5] Giintelberg, *Z. physik. Chem.*, 123, 199 (1926).

[6] Noyes and Ellis, THIS JOURNAL, 39, 2532 (1917).

[7] Åkerlöf, *ibid.*, 48, 1160 (1926).

gam quite rapidly through the stopcocks SS. The second way was to form pools of mercury in the electrode vessels by removing the amalgam comparatively slowly at first through SS. The jets from the capillaries were allowed to flow without breaking into the pools of amalgam. This allowed a large amalgam surface. When using potassium and sodium amalgams *both these methods of manipulation gave identical results.* Owing to the high reactivity of lithium amalgam, the pool method was never successful. The first method of the free flowing jet was always employed, but even this was difficult because of the manner in which the lithium amalgam stuck to the sides of the glass walls. Although results were obtainable which could be reproduced to within ±0.3 mv., they were always somewhat erratic. Other forms of amalgam reservoirs with specially designed capillary delivery tubes were tried but none of these was sufficiently applicable to warrant further description. Such a specially designed apparatus was used in the case of some of the lithium chloride cells.

Experimental Results

1. Potassium Chloride.—The most extensive series of measurements was obtained with the cells containing potassium chloride. The three amalgam reservoirs as well as the three types of silver–silver chloride electrodes were employed. In Table I are given the results with the crystalline silver chloride electrodes of Type 1. Two series were obtained without changing the silver chloride electrodes. One compartment of the cell was filled with 0.1 *M* potassium chloride and the other compartment contained the solutions of varying strengths. The first series was started

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

$Ag \mid AgCl \mid KCl(m) \mid K_xHg \mid KCl(0.1) \mid AgCl \mid Ag$

Type 1. Silver–silver chloride electrodes. $t = 25°$

m	No. 1	No. 2	No. 3	Δ_I (mv.)	No. 1	No. 2	No. 3	Δ_{II} (mv.)	M_I	M_{II}	*M*	A (mv.)
0.01	−0.10885	−0.10902	−0.10906	0.21	−0.10909	−0.10919	−0.10912	0.10	−0.10898	−0.10913	−0.10906	0.15
.02	− .07562	− .07558	− .07569	.11	− .07550	− .07561	− .07556	.11	− .07563	− .07556	− .07559	.06
.05	− .03220	− .03228	− .03227	.08	− .03227	− .03233	− .03227	.06	− .03225	− .03229	− .03227	.04
.1	.00000	.00000	.00000	.00	.00000	.00000	.00000	.oo	.00000	.00000	.00000	.00
.2	.03199	.03196	.03201	.05	.03197	.03202	.03193	.09	.03199	.03197	.03198	.02
.5	.07394	.07397	.07389	.08	.07391	.07387	.07381	.10	.07393	.07387	.07390	.06
1	.10562	.10555	.10556	.07	.10558	.10564	.10562	.06	.10558	.10561	.10559	.03
2	.13888	.13880	.13880	.08	.13880	.13876	.13876	.04	.13883	.13877	.13880	.06
3	.15993	.15962	.15983	.31	.15981	.15984	.15972	.12	.15979	.15979	.15979	.00
4	,17537	.17556	.17547	.19	.17539	.17546	.17545	.07	.17547	.17543	.17545	.04

with the solutions of the lowest concentration and three measurements were taken with the three different amalgam droppers (denoted by Nos. 1, 2 and **3)**. The solution of the next concentration was then introduced and three measurements were taken. This was repeated through Series I, Then the process was reversed and measurements were taken first with the most concentrated and then with the solution of the next lower strength. The second, third and fourth columns contain the electromotive forces of Series I and the next column the total deviation of this series. Series 11 is exactly similar. The columns headed M_{I} and M_{II} are the mean values of the first and second series, respectively, and A is the total deviation of these mean values. The next to last column contains the mean of all the results.

The results of cells containing the 0.01 or 0.02 molal solutions were much more difficult to obtain. The electromotive force of the 0.01–0.1 M cell checked the values obtained by MacInnes and Parker fairly closely. There is considerable doubt as to whether these results are correct. Indeed, Lewis and Randall thought that unavoidable side reactions caused difficulties with these cells, and this opinion has been borne out by more recent investigations. Care therefore should be exercised in attempting to employ these results. On the other hand, the entire cell mechanism works more steadily with solutions of 0.05 M and above so that this series is reliable at concentrations of 0.1 M and higher. The average deviation between Series I and II in the concentration range of from 0.02 to 4 M is 0.04 mv. This is good if it is possible to obtain the same result with other types of silver-silver chloride electrodes.

Table II contains the electromotive forces of the same cells obtained with Type 2 and Type **3** electrodes as well as the mean values of the results with Type 1 electrodes. Those with Type 3 electrodes were obtained by Harned and Douglas and were only single measurements. The measurements obtained with Type 2 electrodes are recent and were made with the

Table II

Electromotive Forces of Cells

Ag | AgCl | KCl(m) | K_xHg | KCl(0.1) | AgCl | Ag

M	Type 3, Noyes and Ellis	No.	Type 2	A (mv.)	Type 1	*M*
0.1	**0.0000**	0	0.00000	..	0.00000	0.00000
.2	.0320	0	.....	..	.03198	.03198
.5	.0739	0	.....	..	.07390	.07390
1	.1056	3	.10570	0.10	.10559	.10565
1.5	....	3	.12459	.08	.....	.12459
2	.1389	3	.13874	.04	.13880	.13877
2.5	....	3	.15018	.07	.....	.15018
3	.1599	3	.15972	.02	.16979	.15976
3.5	....	3	.16772	.11	.....	.16772
4	.1755	3	.17538	.08	.17545	.17541

three different amalgam droppers. A freshly prepared spiral electrode which had been equilibrated with the cell solution for about two hours was used for each measurement. In Col. 3 the number of results obtained with electrodes of Type 2 are given and in Col. 5 their total deviation in millivolts. It is to be observed that the difference in millivolts between the series with Type 1 and Type 2 silver–silver chloride electrodes is 0.11, 0.06, 0.07 and 0.07 mv. in the cells containing the 1, 2, 3 and 4 M solutions, respectively. The results with Type 2 electrodes are all slightly lower than those with Type 1. Further, the agreement with the Noyes and Ellis electrodes (Type 3) is very good.

2. Potassium Bromide, Sodium Chloride and Sodium Bromide.—Cells containing potassium bromide have been previously measured by Pearce and Hart[1d] and Harned and Douglas.[1e] A few results of less accuracy were obtained by Allmand and Polack[1c] from measurements of cells containing sodium chloride. Harned and Douglas also measured the cells containing sodium bromide. The measurements given in Table III are far more extensive and accurate than those previously obtained. Spiral electrodes of Types 2 and 3 were employed. Type 2 electrodes were employed in the case of all three salts. Type 3 or the Noyes and Ellis type were employed in the case of some of the sodium chloride results. This is indicated in the table. A freshly made silver–silver chloride or silver–silver bromide electrode was used in each run of three results.

These electrodes were placed in the cells and in the cell solutions for periods of from three to five hours before readings were taken. In the case of the silver-silver chloride electrodes constant and reproducible values were obtained within two to three hours. Silver–silver bromide electrodes took somewhat longer to equilibrate. For example, cells of the type

$$H_2 \mid HBr \mid AgBr \mid Ag$$

take about four hours to reach a constant and reproducible electromotive force. This remains constant for from four to ten hours and then slowly decreases. In the present investigation the solution and electrode were kept in contact from four to five hours before the first measurement. Removal of the solution and immediate refilling could be carried out without considerably affecting the electromotive force. Consequently, the second and third measurements were carried out within ten to twenty minutes after the first one.

The first column of the table gives the molal salt concentrations, the columns headed "No." contain the number of determinations, the columns E contain the mean electromotive forces and those headed A (mv.) the total deviations in millivolts. In the case of potassium bromide these results check those obtained by Harned and Douglas well at the lower concentrations. Thus they obtained —0.0324, 0.0746, 0.1068, 0.1266 and 0.1410 at concentrations of 0.05, 0.5, 1, 1.5 and 2 molal, which compare favor-

TABLE III

ELECTROMOTIVE FORCES OF THE CELLS Ag | AgX | MX(m) | M_xHg | MX(0.1) | AgX | Ag CONTAINING POTASSIUM BROMIDE, SODIUM CHLORIDE AND SODIUM BROMIDE. $t = 25°$

	MX = KBr; M = K			MX = NaCl; M = Na			MX = NaBr; M = Na		
m	No.	E	A (mv.)	No.	*E*	A (mv.)	No.	*E*	A (mv.)
0.05	9	−0.03232	0.14	.	.....	..		.....	..
0.1	.	.00000	..	.	0.00000	..	.	0.00000	..
0.2	6	.03214	.20	8	.03247	0.19	6	.03274	0.12
0.5	6	.07455	.13	6	.07566	.15	6	.07691	.11
1	6	.10687	.09	6	.10957[a]	.14	6	.11183	.11
1.5	3	.12620	.02	10	.13033[a]	.16	6	.13332	.24
2	6	.14045	.17	9	.14621[a]	.20	6	.15070	.21
2.49	3	.15162	.08	.	.....	..		.....	..
2.5	3	.15193	.10	3	.15923	.15	6	.16500	.31
3	9	.16143	.31	6	.17037	.07	6	.17756	.22
3.5	5	.17008	.20	3	.18188[b]	.10	6	.18842	.30
4	6	.17784	.26	6	.19079[a]	.08	6	.19877	.23

[a] Three were obtained with Type 3 electrode.

[b] One was obtained with Type 3 electrode.

ably with those given in Table III. In the case of the cells containing sodium bromide, they obtained 0.0773, 0.1123, 0.1345, 0.1505, 0.1659 and 0.1779 at 0.5, 1, 1.5, 2, 2.5 and 3 molal salt concentrations, which agree fairly well with the later results. The total deviations of the results are seen to be within 0.3 millivolt. We regard this as very good since the cell mechanism is complicated, since the conditions of flow of the amalgam were varied in each case and since new silver–silver halide electrodes were made for each run of three or less results. It has been our experience that results of very high consistency may be obtained by performing each operation in exactly the same manner. We do not believe that results thus obtained are necessarily the correct reversible electromotive forces. We have, therefore, preferred to sacrifice consistency by varying the cell mechanism in the ways previously described.

3. Lithium Chloride and Bromide.—In Table IV are given the results obtained with lithium amalgams. Since we were never able to obtain as steady readings with these as with the sodium or potassium amalgams, we regard the results as having approximately an accuracy of ± 0.2 mv. up to 2 molal. In the case of cells containing salt at higher concentrations than this, the accuracy decreases. We obtained 0.1168 and 0.1958 volt with cells containing lithium chloride at 1 and 3 molal concentrations, respectively, which agree fairly well with 0.1165 and 0.1954 previously determined by MacInnes and Beattie. Since all the electrodes were prepared in an entirely different manner from that employed by these investigators, the result is encouraging.

One possible source of error which is independent of the mechanism and operation of these cells remains to be discussed. In concentrated

TABLE IV

ELECTROMOTIVE FORCES OF THE CELLS $Ag \mid AgX \mid MX(m) \mid M_4Hg \mid MX(0.1) \mid AgX \mid Ag$ CONTAINING LITHIUM CHLORIDE AND LITHIUM BROMIDE. $t = 25°$

		MX = LiCl; M = Li			MX = LiBr; M = Li	
m	No.	*E*	A (mv.)	No.	*E*	A (mv.)
0.1	.	0.0000	0.0	4	0.0000	0.0
.2	5	.0336	.1	4	.0340	.2
.5	3	.0790	.2	3	.0803	.3
1	3	.1168	.2	3	.1191	.1
1.5	1	(.1417)	...	3	.1444	.6
2	3	.1624	.4	3	.1657	.2
2.5	1	(.1802)	...	3	.1845	.3
3	3	.1958	.5	3	.1998	1.0
3.5	1	(.2112)	...	3	.2160	1.0
4	3	,2250	.2	3	.2324	1.3

In the lithium chloride series the results in parentheses were found with Type 2 silver–silver chloride electrodes. All others were made with Type 1 electrodes. All lithium bromide results were obtained with Type 2 electrodes.

salt solutions the solubility of the silver halides increases rapidly with the salt concentration. The solubility of silver chloride in potassium, sodium and lithium chlorides is not sufficient to cause any error greater than the experimental error of these measurements. On the other hand, the solubility of silver bromide in the corresponding salt solutions is sufficient to cause an error in the solutions of 2 M salt concentration and higher. Thus, from the data of Hellwig,[8] we find that in a 3 M potassium bromide solution enough silver bromide will be dissolved to cause a maximum error of 0.3 mv. either by reason of its adding bromide ion to the solution or removing bromide ion due to complex formation. This error will be greater in the cases of sodium and lithium bromides. We do not believe that the amalgam electrodes were affected by any silver which may have diffused into the amalgam compartment of the cells. This was shown by the fact that the solution could be removed from the cell, a fresh one introduced and the same result obtained from a measurement taken before diffusion could have taken place. The effect of the solubility of silver iodide in the iodide solutions upon the electromotive force of such cells was pointed out by Harned and Douglas to be of such a magnitude as to render the result uncertain when the iodide solutions were more concentrated than 1 molal.

A Discussion of the Electromotive Forces of Halide Solutions.—In Table V, Part I, the electromotive forces of concentration cells without liquid junction containing the electrolyte at 0.1 M and 1 M concentrations in the two compartments are compiled.

As a first attempt to consider these results, MacInnes[g] and Harned[10]

---

[8] Hellwig, *Z. anorg.* Chem., 25, 183 (1900).

[9] MacInnes, THIS JOURNAL, 41, 1086 (1919).

[10] Harned, *ibid.*, 42, 1808 (1920).

TABLE V

PART I. ELECTROMOTIVE FORCES OF THE CELLS

$Ag \mid AgX \mid MX(1) \mid M_xHg \mid MX(0.1) \mid AgX \mid Ag$

$Ag \mid AgX \mid HX(1) \mid H_2 \mid HX(0.1) \mid AgX \mid Ag$

M = Li, Na or K X = Cl, Br or I

Electrolyte	KCl	NaCl	LiCl	HCl	KBr
E	0.10565	0.10957	0.1168	0.1195[a]	0.10687
Electrolyte	NaBr	LiBr	HBr[b]	KI[c]	NaI[c]
E	0.11183	0.1191	0.1227	0.1092	0.1147

[a] Scatchard, THIS JOURNAL, **47**, 2098 (1925); Harned, *ibid.*, **48**, 326 (1926).

[b] Unpublished measurements obtained with air-free HBr solutions by Dr. Geoffrey M. James.

[c] Harned and Douglas, ref. le.

PART II. DIFFERENCES IN MILLIVOLTS OF ABOVE CELLS

$\Delta = E_{KBr} - E_{KCl}, E_{NaCl} - E_{KCl}$, etc.

		A		A	
	KCl	1.3	KBr	2.3	KI
A	4.0		5.0		5.5
	NaCl	2.2	NaBr	2.9	NaI
A	7.2		7.3		
	LiCl	2.3	LiBr		...
A	2.7		3.6		
	HCl	3.2	HBr		...

PART III. SIMILAR DIFFERENCES FOR CELLS CONTAINING 0.1 *M* AND 2 *M* SALT CONCNS.

KCl	1.7	KBr	4.2	KI
7.4		10.3		
NaCl	4.5	NaBr		...
16.2		14.4		
LiCl	3.3	LiBr		...
3.9		8.2		
HCl	7.0	HBr		...

proposed a tentative postulate which was the equivalent of the assumption that the electromotive forces of the cells under discussion referred to a given concentration should be additive. We are now able to show that this postulate is only a rough approximation, and point out the character of the departure from this postulate. In Part II of Table V are given the differences in millivolts of the cells containing the different salts. Although the differences between bromides and chlorides, sodium and potassium salts, etc., are of the same order of magnitude, there appears to be a uniform deviation from a strict additive relationship.

On the other hand, the deviation is not uniform in the cases of the more concentrated solutions, if we can rely on the results obtained for the cells containing lithium salts. This is illustrated by Part III of the table. Thus it is seen that the difference between lithium and sodium chlorides is greater than that between the corresponding bromides.

The Activity Coefficients of Halides.—In order to obtain the activity coefficients of potassium and sodium chlorides and bromides from the results in Tables II and III we have made use of the method of extrapolation employed by Hückel.[11] By means of the equation

---

[11] (a) Hückel, *Physik. Z.*, **26**, 93 (1925); (b) Scatchard, THIS JOURNAL, **47**, 2098 (1925); (c) Harned, *ibid.*, **48**, 326 (1926); (d) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

$$\log \gamma = -\frac{0.356\sqrt{2c}}{1 + A\sqrt{2c}} + B \times 2c - \log (1 + 0.036\ m) \qquad (1)$$

where c is the concentration in normality, m the molal concentration and A and B are constants, it is possible to extrapolate to infinite dilution the data at higher concentrations with a considerable degree of certainty. Having evaluated the constants A and B, the activity coefficients, γ, obtained by Equation 1 may be compared with those obtained from the electromotive force data according to the thermodynamic equation of the cells. Since the results were all obtained by the use of the 0.1 M reference solution, this latter equation is

$$E = 0.1183 \log \frac{\gamma m}{\gamma_{0.1} \times 0.1} \qquad (2)$$

where $\gamma_{0.1}$ is the activity coefficient in 0.1 M solution. The results obtained by the use of these two methods are compiled in Table VI. The values, $\gamma_{\text{obs.}}$, are the activity coefficients computed directly from the electromotive force data by Equation 2, employing the reference values in parenthesis at 0.1 M, and $\gamma_{\text{calcd.}}$ are those computed by Equation 1. The values of A and B employed are given in the lower part of the table.

TABLE VI

CALCULATION OF ACTIVITY COEFFICIENTS OF POTASSIUM AND SODIUM CHLORIDES AND BROMIDES BY HÜCKEL'S EQUATION

m	$\gamma_{\text{obs.}}$(KCl)	$\gamma_{\text{calcd.}}$(KCl)	$\gamma_{\text{obs.}}$(KBr)	$\gamma_{\text{calcd.}}$(KBr)	$\gamma_{\text{obs.}}$(NaCl)	$\gamma_{\text{calcd.}}$(NaCl)	$\gamma_{\text{obs.}}$(NaBr)	$\gamma_{\text{calcd.}}$(NaBr)
0.001	0.965	0.965	...	...	0.966	0.965	....	...
.005	.926	.927	...	...	.928	.928	....	...
.01	.899	.901	...	...	.903	.903	....	...
.05	.815	.815	0.816	0.815	.821	.819	0.824[a]	0.822
.1	(.764)	.764	(.765)	.766	(.778)	.775	(.779)	.780
.2	.712	.7115	.715	.715	.732	.729	.737	.737
.5	.644	.643	.653	.651	.678	.678	.696	.694
1	.597	.598	.612	.612	.656	.658	.687	.689
1.5	.576	.579	.595	.597	.658	.662	.696	.699
2	.569	.569	.589	.591	.670	.674	.732	.732
2.5	.568	(.564)	.589	.589	.690	.692	.773	(.752)
3	.571	(.561)	.590	(.587)	.714	.715	.823	(.785)
3.5	.571	(.561)	.599	(.594)	.749	(.739)	.871	...
4	.581	(.574)	.609	(.598)	.779	(.764)	.933	...
	$A = 0.76$		$A = 0.78$		$A = 0.84$		$A = 0.88$	
	$B = 0.0171$		$B = 0.0204$		$B = 0.032$		$B = 0.0383$	

[a] **Harned** and Douglas, **ref.** le.

In our previous computations these constants were obtained from the electromotive forces of the cells at 0.1, 1 and 3 molal concentrations. This elaborate calculation has not been repeated. The B constants of the previous calculations have been changed somewhat to meet the requirements of the new experiments in the concentration range from 0.1 to 2 molal. The values for potassium and sodium chloride at 0.001, 0.005 and 0.01 molal taken from the compilation of Scatchard were obtained by him from freezing point data.[12]

Up to a concentration of 2 *M* the agreement between the observed and calculated values is extraordinarily good. The difference between the values obtained is rarely over two in the third place of activity coefficient, which corresponds to a deviation of a little over 0.1 mv. At concentrations above 2 M the values obtained by Hiickel's equation are all somewhat less than the observed values and this difference increases with increasing salt concentration.

In the cases of the less accurate results with lithium chloride and bromide, we have made no further calculation by Equation 1 but have simply computed γ by Equation 2. To this end we employed the reference values at 0.1 M indicated by parenthesis in Table VII. Some of them had been previously obtained by extrapolation by Equation 1.[11a,d] In the case of the less accurate results with the iodides, suitable values were chosen at 0.1 M concentration. In this table we have also included the activity coefficients of hydrochloric acid as recently computed by Randall and Young,[13] hydrobromic acid computed from the results of James[14] and potassium and sodium iodides obtained from the data of Harned and Douglas.[1e]

TABLE VII

THE ACTIVITY COEFFICIENTS OF HALIDES IN CONCENTRATED SOLUTIONS

m	γ_{LiCl}	γ_{LiBr}	γ_{HCl}	γ_{HBr}	γ_{KI}	γ_{NaI}
0.01	0.901	...	0.904	0.906	...	...
.05	.819	...	.829	.831	.820	...
.1	(.779)	(0.794)	(.796)	(.802)	(.775)	(0.788)
.2	.756	.769	.766	.779	.730	.754
.5	.725	.758	.757	.788	.678	.721
1	.757	.806	.810	.873	.649	.734
1.5	.819	.890	.903	...	.646	...
2	.919	.999	1.019	1.169	.646	...
2.5	1.040	1.152	1.151	...	...	...
3	1.174	1.293	1.320	1.671	...	...
3.5	1.358	1.519	1.520	...	...	...
4	1.554	1.829	1.762	...	...	...

The character and distribution of the results are shown in Fig. 2, where γ is plotted against $\mu^{1/2}$.

Comparison of Activity Coefficients Obtained from Electromotive Force and Vapor Pressure Data.—It is a matter of considerable impor-

---

[12] Scatchard, THIS JOURNAL, 47, 648 (1925).

[13] Randall and Young, *ibid.*, 50,989 (1928).

[14] James, unpublished results.

tance to verify the above method for determining activity coefficients by comparing the values thus obtained with values computed by another method which involves a different experimental mechanism. To this end, the vapor pressure measurements of Lovelace, Frazer and Sease[15] of solutions of potassium chloride at 20° are suitable. Since the vapor pressure measures the activity of the solvent, it is possible to compute the activity of the solute by the equation

$$\partial \ln a_2 = -\frac{N_1}{N_2}\partial \ln a_1 \qquad (3)$$

where a_1, N_1 and a_2, N_2 are the activities and mole fractions of the solvent and solute, respectively. If the vapor pressure of the solvent is not great, the gas laws will hold for the vapor, and the vapor pressure, p_1, may be taken as proportional to α_1. Consequently, by substituting p_1 for α_1 and forming a definite integral, we obtain

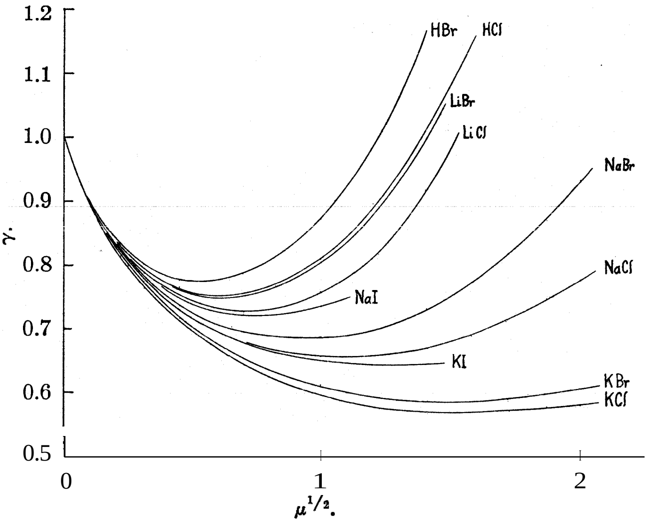


Fig. 2.

$$\int_{\alpha_2'}^{\alpha_2''}\partial \ln \alpha_2 = -\int_{p_1'}^{p_1''}\frac{N_1}{N_2}\partial \ln p_1 \qquad (4)$$

By plotting N_1/N_2 against $\ln p_1$ and evaluating the integral on the right graphically, $\ln \alpha_2''/\alpha_1'$ or $\ln \gamma_2 m_2/\gamma_1 m_1$ may be obtained. From this γ relative to a given concentration may be computed. A similar computation has been made by Scatchard.[16] In Table VIII the result of this calculation is given. The values at 1 M were taken to be identical at the two temperatures. The agreement at 0.2 and 0.5 molal is excellent but

---

[15] Lovelace, Frazer and Sease, THIS JOURNAL, 43, 102 (1921).

[16] Scatchard, *ibid.*, **47**, 654 (1925).

TABLE VIII

COMPARISON OF ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE FROM ELECTROMOTIVE FORCE AND VAPOR PRESSURE DATA

m	0.1	0.2	0.5	1	2	3	4
γ (E.m.f.) 25°	0.764	0.712	0.644	(0.597)	0.569	0.571	0.581
γ (V. P.) 20°	(0.780)	0.713	0.643	(0.597)	0.566	0.562	0.565

at 0.1 molal the result is not good. This is probably due to an error in the vapor pressure method. At 2, 3 and 4 molal the values at 20° become increasingly less than those at 25°. This is to be expected since the partial molal heat of dilution is negative. The magnitude of the difference is of the correct order.[17] We regard this agreement in the concentration range of from 0.2 to 4 molal as excellent confirmation of the method employed.

I take this opportunity to express my appreciation to Dr. Geoffrey M. James and Mr. Robert Robinson for the valuable assistance rendered by them at the time of these measurements.

Summary

1. Measurements at 25° of high accuracy of cells of the type

$$Ag \mid AgX \mid MX(m) \mid M_xHg \mid MX(0.1) \mid AgX \mid Ag$$

containing sodium and potassium chlorides and bromides have been made.

2. Similar but less accurate measurements have been made with similar cells containing lithium chloride and bromide.

3. The electromotive forces of halides have been discussed and considerable departure from additivity is observable.

4. The activity coefficients of sodium and potassium chlorides and bromides have been calculated from the results of the electromotive force measurements and compared with those calculated by Hückel's equation.

5. The activity coefficients of ten halides have been calculated and discussed.

6. The activity coefficients of potassium chloride derived from the electromotive force measurements have been compared with those computed from vapor pressure measurements.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

---

[17] See Harned, THIS JOURNAL, 44, 252 (1922).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

KINETIC STUDIES ON ETHYLENE OXIDES

BY J. N. BRÖNSTED, MARY KILPATRICK AND MARTIN KILPATRICK

RECEIVED OCTOBER 6, 1928 PUBLISHED FEBRUARY 5, 1929

A. Introduction

The ethylene oxides form a group of compounds which is of great interest from the standpoint of both organic and physical chemistry. Their exceptional reactivity in solution already at ordinary temperature offers an inviting field for multifarious kinetic investigations. The "basicity" of these compounds in particular is a striking phenomenon, the mechanism of which does not seem as yet to have been fully understood.

In textbooks of organic chemistry the ethylene oxides are sometimes referred to as "pseudo bases." It is generally recognized that they cannot be classed as bases in the usual sense of this word owing to their lack of electric conductivity in pure aqueous solution. It also seems to be a general opinion that "basicity" of the substances is explicable from their tendency to unite with acids. The precipitation of insoluble metallic hydroxides, e. g., ferric hydroxide, from solutions of the corresponding salts is then looked upon as due to reactions with the acid made free by "hydrolysis."

It will be shown in the present paper that this addition of acids exhibited by the ethylene oxides is kinetically only to a minor extent the reason for their apparent basicity. Regardless of this fact, however, it should be realized that the ability of a substance to add an acid is by no means a feature characteristic of bases. Bases are characterized by adding protons. Taking up the whole of an acid molecule is something quite different from the basic function; it depends upon the anion of the acid in an individual manner and need not have any relation to the strength of the acid added. For instance, the strongest of all electrically neutral acids, perchloric acid, does not react with ethylene oxides in the same way as do the hydrohalogenic acids, although in this group the addition velocity increases with the strength.

Hantzsch[1] was the first to study the reaction between ethylene oxides and acids from a physico-chemical standpoint. He found by conductivity measurements that hydrochloric acid is taken up by ethylene oxide with a considerable velocity, but the reaction came to a standstill long before all of the acid or oxide had disappeared. He did not give any explanation of the incompleteness of the reaction, However, at the same time Henry[2] showed that the oxides in the presence of acids take up water to form

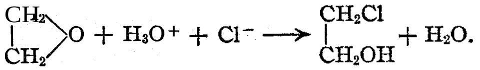
---

[1] Hantzsch and Hibbert, *Ber.*, **40**, 1,514 (1907).

[2] Henry, *Compt. rend.*, **144**, 1404 (1907).

glycols. The part of the oxide reacting in this way is of course prevented from combining with the hydrochloric acid and this easily explains the result of Hantzsch.

The most obvious manner in which hydrochloric acid in dilute aqueous solution may react with ethylene oxide is kinetically as follows



$$\begin{array}{l}CH_2\\ |\;\;\rangle O\\ CH_2\end{array} + H_3O^+ + Cl^- \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} + H_2O.$$

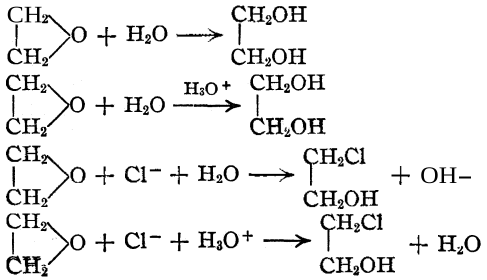
As it stands it presents a reaction between an electrically neutral molecule and two ions of opposite sign and accordingly from the theory of velocity of ionic reactions[3,4] the velocity should be given by

$$h = kc_{Ox}\cdot c_{H_3O^+}c_{Cl^-}f_1^2 \tag{1}$$

the c's indicating the concentrations of the reacting molecules and f the activity coefficient of a univalent ion. A reaction like this might, therefore, be well suited for testing the theory of reaction velocity. In fact, the work described in the present paper was taken up with the primary purpose of providing such a test.

What happens in an aqueous solution of ethylene oxide in the presence of hydrochloric acid is, however, more complicated than the simple addition of the acid. It has already been mentioned that the oxide takes up water when acids are present. This is a hydrogen-ion catalysis. Furthermore, there is a "spontaneous" water addition. Finally, we have found that the oxide combines with the anion of the acid and water, a reaction which is independent of hydrogen-ion concentration. There may also be acid catalysis in the general sense of this term,[5] but this we have been unable to detect with certainty so far,

In other words, ethylene oxide in a solution of hydrochloric acid disappears by four different paths, as follows:



Reaction I $$\begin{array}{l}CH_2\\ |\;\;\rangle O\\ CH_2\end{array} + H_2O \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

Reaction II $$\begin{array}{l}CH_2\\ |\;\;\rangle O\\ CH_2\end{array} + H_2O \xrightarrow{H_3O^+} \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

Reaction III $$\begin{array}{l}CH_2\\ |\;\;\rangle O\\ CH_2\end{array} + Cl^- + H_2O \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} + OH^-$$

Reaction IV $$\begin{array}{l}CH_2\\ |\;\;\rangle O\\ CH_2\end{array} + Cl^- + H_3O^+ \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} + H_2O$$

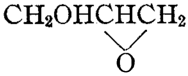
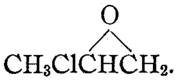
The reactions not only take place with the simple ethylene oxide, but are probably general for the whole group of oxides. In addition to the

---

[3] Bronsted, *Z. physik. Chem.*, *102*, **169** **(1922).**

[4] Brönsted and Livingston, THIS JOURNAL, 49, 435 **(1927).**

[5] Brönsted, *Chem. Reviews*, 5, *312* **(1928).**

simple oxide, we investigated glycid,  $CH_2OHCHCH_2$ and epichlorohydrin,  $CH_3ClCHCH_2$. Furthermore, hydrochloric acid can be replaced by a great number of other acids.

For the sake of simplicity the reactions will henceforth be referred to by the numbers assigned to them above.

B. Preparations

a. Ethylene Oxide.—Ethylene chlorohydrin, CH_2ClCH_2OH, was made from ethylene glycol by the method of Ladenburg.[6] A 25% solution of sodium hydroxide was admitted slowly from a dropping funnel onto ethylene chlorohydrin contained in a distilling flask in a water-bath at 50–60°. The side arm of the distilling flask was attached to a spiral condenser packed in an ice and salt freezing mixture and the tube of the condenser passed into a receiving bulb similarly cooled. The distillation of ethylene oxide proceeded slowly, taking four hours for an 80-g. portion of chlorohydrin; at the end of this time the temperature of the water-bath was raised to 80°. The contents of the receiving bulb were then redistilled directly into a storage tube packed in ice and salt in a Dewar flask. The greater part of the ethylene oxide passed over at 12–13", as recorded by a thermometer, the bulb of which was immersed in the liquid oxide; this was the fraction used. The pure, dry oxide boils at 10.7° according to Maass and Boomer.? For our purpose, however, it was unnecessary to go through the tedious process of entirely removing the water.

b. **Glycid.**—α-Monochlorohydrin, $CH_2ClCHOHCH_2OH$, was made by passing hydrogen chloride into glycerin under the conditions of Smith's "Synthesis 2."[8] Nef's method[9] was used in the preparation of glycid from α-monochlorohydrin. After several fractionations of our product we obtained a quantity of glycid corresponding to 37% of the theoretical yield, free from any chlorine-containing impurity, boiling between 55 and 57° at 8–10 mm. pressure and of specific gravity 1.115^{20}_{4}. The specific gravities previously recorded are[g] 1.111^{22} and[10] 1.165".

c. **Epichlorohydrin.**—For our experiments with epichlorohydrin we redistilled Kahlbaum's epichlorohydrin and took that fraction boiling between 116.5 and 117.5° at 765 mm.

C. Reactions I and II

It was found by Wurtz,[11] Nef[g] and Reboul[12] that the three oxides in question in the presence of water at 100° slowly transform into the corresponding glycols. Reaction I must then be very slow at ordinary temperature. In the case of oxides containing a tertiary carbon atom

---

[6] Ladenburg, *Ber.*, 16, 1407 (188'3).

[7] Maass and Boomer, THIS JOURNAL, 44, 1709 (1922).

[8] Smith, Z. *physik. Chem.*, 94, 696 (1920).

[9] Nef, *Ann.*, 335, 231 (1904).

[10] Beilstein, "Handbuch der organischen Chemie," 3d ed., Vol. I, p. 313. The specific gravity (20°/4°) is given in "International Critical Tables," Vol. I, p. 183, as 1.165; this seems to be an error.

[11] Wurtz, *Ann.*, 113, 255 (1860).

[12] Reboul, *ibid.*, Suppl. I, 233 (1861).

the hydration proceeds much faster.[13] Our measurements of the rates are described below.

It has been mentioned that the addition of water to the oxides is accelerated by acids. It is, however, only recently that these reactions have been studied as examples of hydrogen-ion catalysis. After the present investigation was begun, Smith, Wode and Widhe[14] published measurements on the rates of addition of water to ethylene oxide and to epichlorohydrin at 25° in solutions of nitric acid and of perchloric acid of concentration 0.01 to 0.3 M. The reactions were followed by analytical methods and especially in the case of ethylene oxide the experimental errors were large. The authors state that, from their results, they are unable to judge whether the rate of reaction is proportional to the hydrogen-ion concentration or to the hydrogen-ion activity. From their results with nitric and perchloric acids, and from some results (as yet unpublished) with sulfuric acid, Smith, Wode and Widhe conclude that the nature of the anion of the catalyzing acid is unimportant.

1. Experimental Method

A dilatometric method was used in the present investigation for following Reactions I and II. From density data it was calculated that the hydration of ethylene oxides is accompanied by a considerable contraction. This was actually found to be the case also in solution, the contraction during reaction of 50 cc. of a solution originally 0.2 *M* in ethylene oxide being about 10 cm., measured in a capillary tube 1 mm. in diameter. Preliminary experiments showed that the conductivity of a solution 0.01 *M* in perchloric acid, or of a solution 0.01 M in perchloric acid and 0.1 M in sodium perchlorate, remained practically constant during the reaction; there was, therefore, no interference of Reactions III or IV. For this reason it was decided to use perchloric acid as catalyst. With the development of an accurate method of measurement it was thought that k_1, the constant of the "spontaneous" reaction (Reaction I), might be obtained by extrapolation of the velocity constants in dilute acid solution.

The apparatus is shown in Fig. 1. A is a vessel of 150-cc. capacity used as a mixing chamber and as conductivity cell; B and C are platinized electrodes; D is *a* tube through which carbon dioxide-free air may be admitted. The bulb E, of 50-cc. capacity, is the diiatometer. FG, the graduated portion of the capillary, is 0.0086 cm^2. in cross section and 20 cm. in length. It was found that the bore of the capillary was uniform to within 1% throughout the entire length and uniform to 0.5% throughout the upper half; the upper half was the region used. T, a glass chamber filled with mercury, is capped with a steel top through which moves the screw H acting as a plunger. With the screw H in its uppermost position mercury stands in the small reservoir K, and with the screw in its lowest position mercury extends to L and M in the tubes to the left

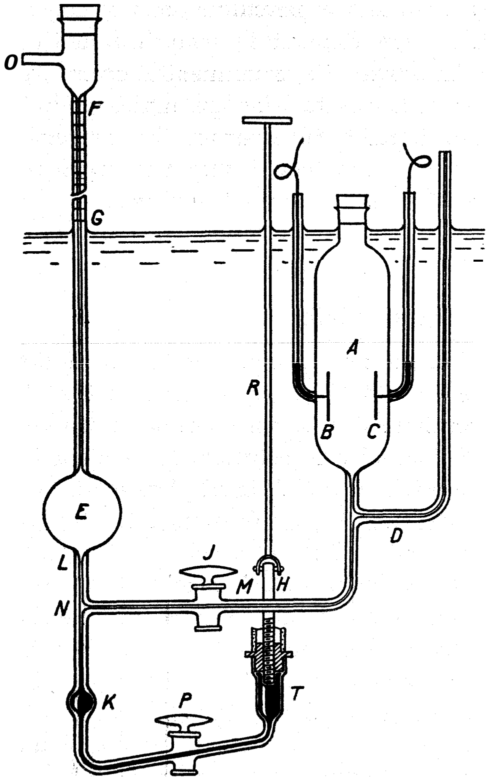
---

[13] Eltekow, *Ber.*, 16, 395 (1883).

[14] Smith, Wode and Widhe, *Z. physik. Chem.*, **130,** 154 (1927).

and right of the cock I. The upper part of the screw, H, and the connecting rod, R. are enclosed in a rubber tube. The apparatus was mounted and placed in an insulated glass thermostat at 20.00°; the maximum fluctuation in temperature observed in the thermostat during the course of the work was 0.005°.

The procedure was as follows: 150 cc. of a solution of ethylene oxide was placed in the cell A and allowed to come to the temperature of the bath. A given volume of the solution was removed with a pipet and the same volume of 0.1 *M* perchloric acid was added. Mixing was effected by bubbling air through the solution for a few minutes. On account of the electrodes it was not feasible to dry the apparatus between experiments and, after draining, a few drops of water always remained in the tubes connecting A and E. One-third of the solution was therefore allowed to flow over into E and was forced back into A by compressed air applied at Q, before the dilatometer was finally filled. During the filling the mercury stood at N. Experience showed that if the solution was drawn up to G in the capillary, and the cock I closed, by alternately screwing down H (cock P open) and opening I, mercury could be brought to the position I, and M, and the solution D to a convenient position near the top of the graduations on the capillary. Cock P was then closed. The mercury-sealed cock[15] J proved very satisfactory and only an occasional regreasing was necessary. The tightness of J was frequently tested by reading the position of the meniscus of a column of water confined in the apparatus at the beginning and at the end of a period of twelve hours. The process of mixing the solution and filling the dilatometer took approximately ten minutes. No trouble was experienced from the formation of air bubbles.



Pig. 1.

Readings were taken at convenient intervals over a period approximately twice the half time of the reaction, and later a second set of readings was taken at the same intervals. The time elapsing between the two sets of readings was always more than twice the period of. half completion; as a rule it was twenty-four hours. The experiments were calculated by the method suggested by Guggenheim.[16]

For very slow reactions, as Reaction I in the case of ethylene oxide, the rate was determined by measuring the contraction in a sealed dilatometer. The dilatometer was a bulb of 50-cc. capacity, from the top of which extended a graduated capillary tube 0.6 mm. in diameter and 30 cm. long, and from the bottom a short thin-walled

---

[15] Brönsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

[16] Guggenheim, *Phil. Mag.*, 1, 538 (1926).

tube. Before filling the dilatometer the lower tube was drawn out each time in the flame. The dilatometer was filled by suction applied through the upper tube, and the lower tube was then sealed off at its narrowest point. If an air bubble formed in the solution during the process of filling or of sealing, it was expelled through the capillary by tilting and tapping while the dilatometer bulb was gently warmed. The solution was protected from the air by a glass cap fitting over the top of the capillary tube and dipping into a mercury-filled cup. The rate was calculated by Guggenheim's method, particularly convenient in the case of very slow monomolecular reactions such as this.

2. Results with Ethylene Oxide

Table I gives the data of a typical experiment to determine the velocity of Reaction II. The concentration of perchloric acid (M here and in the following means molarity, i. e., moles per liter) recorded is the mean of the value calculated from dilution of a standard solution of perchloric acid and the value found by titration of 100 cc. of the residual solution against standard sodium hydroxide at the end of the experiment. The perchloric acid concentration given in all the experiments represents this mean. The difference between the two values was always small, and sometimes positive, sometimes negative. The resistance of the solution was measured at intervals during the course of the reaction. With perchloric acid and perchlorates there was usually an increase in resistance of about 0.5%; the

TABLE I

HYDRATION OF ETHYLENE OXIDE. A TYPICAL EXPERIMENT. $t = 20°$

Ethylene Oxide, 0.12 M. $HClO_4$, 0.007574 M. $0.4343k = 0.001070$

Time, min.	Dilatometer reading	Reading 24 hrs. later	Δv	Log Δv	Δv, calcd.	Deviation
0	18.48	12.40	6.08	0.784	6.08	0.00
15	18.27	12.395	5.875	.769	5.86	+0.015
30	18.05	12.39	5.66	.753	5.66	0.00
45	17.83	12.39	5.44	.736	5.44	0.00
60	17.62	12.38	5.24	.719	5.25	−0.01
75	17.43	12.375	5.055	.704	5.06	−0.005
90	17.25	12.37	4.88	.688	4.875	+0.005
105	17.07	12.365	4.705	.673	4.71	−0.005
120	16.89	12.36	4.53	.656	4.53	0.00
135	16.71	12.35	4.36	.640	4.37	−0.01
225	15.83	12.32	3.51	.545	3.51	0.00
240	15.70	12.315	3.385	.530	3.38	+0.005
255	15.58	12.31	3.27	.515	3.26	+0.01
270	15.47	12.305	3.165	.500	3.14	+0.025
285	15.34	12.30	3.04	.483	3.035	+0.005
300	15.22	12.30	2.92	.465	2.92	0.00
315	15.11	12.295	2.815	.450	2.82	−0.005
330	15.00	12.29	2.71	.433	2.71	0.00
345	14.90	12.29	2.61	.417	2.61	0.00
360	14.80	12.29	2.51	.400	2.525	−0.015
375	14.71	12.29	2.42	.384	2.43	−0.01
390	14.62	12.29	2.33	.367	2.34	−0.01

effect upon the resistance of the change in medium with the progress of the reaction will be discussed in a later section of the paper. The fourth column of the table gives Av or the difference between the reading in the second column and the corresponding reading in the third column. When log *Av* is plotted against the time, recorded in Col. 1, the slope of the best line drawn through the points is **—0.4343** k. The fifth column shows the values of Av, of which the logarithms lie exactly on this line, and *Av* — $\Delta v_{\text{calcd.}}$ gives the deviation of any point from the line.

Experiments were made in solutions of perchloric acid ranging in concentration from **0.003** to **0.02 M.** The velocity constants are given in the sixth column of Table **II,** and in Fig. **2** they are shown plotted against the concentration of perchloric acid.

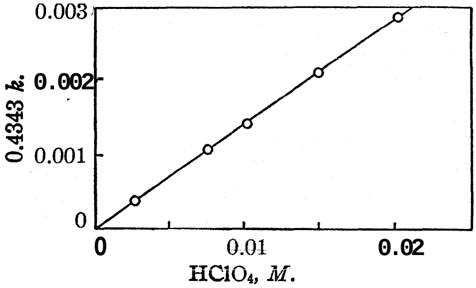


Fig. 2.—Effect of hydrogen ion upon the velocity of addition of water to ethylene oxide (Reaction II).

From **Fig.** 2 it is obvious that the observed velocity constants lie approximately on a straight line. It is evident, therefore, that the rate of reaction is proportional to the hydrogen-ion concentration. From the figure it is also evident that, without carrying out tediously long experiments in very dilute acid solution, it is futile to hope to detect, much less to measure, the spontaneous reaction (Reaction I) by extrapolation of the results in acid solution. It is also evident that the spontaneous reaction can have only a very slight effect upon the rates here measured.

In order to determine the spontaneous reaction the sealed dilatometer was employed, the measurement extending over a period of two months. The solution used was prepared from ethylene oxide and carbon **dioxide-free** water to which a drop of dilute sodium hydroxide solution was added; the resulting solution was **0.2** M in oxide and just alkaline to bromthymol

TABLE II

EFFECT OF HYDROGEN ION UPON THE RATE OF ADDITION OF WATER TO ETHYLENE OXIDE. SALT EFFECT. $t = 20°$. $0.434k_1 = 9.4 \times 10^{-6}$

Molarity, oxide	Molarity, $HClO_4$	Molarity, $NaClO_4$	ΔR, %	Total equiv. salt concn.	0.4343 k, obs.	0.4343 k_2
0.17	0.00272	0	-0.4	0.003	0.000385	0.138
.12	.007574	0	— .3	.008	.001070	.1401
.15	.01015	0	+0.2	.010	.001434	.1404
.17	.01496	0	0	.015	.002130	.1418
.11	.02017	0	+0.4	.020	.002868	.1417
.18	.01015	0.046	+ .6	.056	.001484	.1453
.20	.01014	.092	+ .7	.102	.001540	.1510
.18	.01493	.092	+ .5	.107	.002283	.1523

blue. The velocity constant, $0.434 k_1$, was found to be 9.4×10^{-6}, corresponding to a half time of 23 days at 20°. The effect of any hydrogen-ion catalysis was negligible in our solution, which at the start was 1×10^{-8} molar in hydrogen ion. Experiments in sodium hydroxide solutions up to 0.1 *M* showed the effect of hydroxyl ion to be negligible also.

Knowing k_1 we can now determine exactly k_2, the constant of Reaction II for molar acid, at various salt concentrations.

The sixth column in Table II records the observed velocity constant, and the seventh shows this constant corrected for the spontaneous reaction and divided by the hydrogen-ion concentration, *i. e.*, $k_2 = (k - k_1)/(\text{molarity } HClO_4)$. The fourth column of Table II gives the percentage change in resistance during the reaction. In Fig. 3 $0.4343 k_2$ is plotted against the total equivalent salt concentration, the salt effect of $NaClO_4$ and $HClO_4$ being taken as equal in the first approximation.

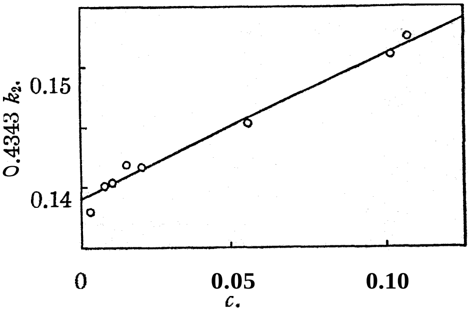


Fig. 3.--Salt effect upon Reaction II. Ethylene oxide, c = total salt concentration $= M_{HClO_4} + M_{NaClO_4}$.

The catalytic constant for ethylene oxide thus may be represented by the linear relationship

$$0.4343 k_2 = 0.1391 4 0.120 c$$

c being the salt concentration. The 9% increase in 0.1 N salt solution is a rather large primary salt effect.

3. Results with Glycid

Reaction I in the case of glycid was followed in a way similar to that described above for ethylene oxide. In Table III are collected the results of experiments in pure water and in various solutions.

TABLE III

THE "SPONTANEOUS" ADDITION OF WATER TO GLYCID. t = 20°

Composition of solution	$0.43 k_1 \times 10^6$
Glycid, 0.1 M, CO_2-free water	6.8
Glycid, 0.1 M, CO_2-free water	6.9
Glycid, 0.1 M, Na_2HPO_4, 0.0025 *M*; KH_2PO_4, 0.0025 *M*	7.6
Glycid, 0.1 *M*, Na_2HPO_4, 0.0050 *M*; KH_2PO_4, 0.0050 *M*	7.0
Glycid, 0.1 *M*, Na_2HPO_4, 0.011 *M*; KH_2PO_4, 0.011 *M*	7.6
Glycid, 0.1 *M*, NaOH, 0.0001 M	8.6
	Average, 7.4×10^{-6}

The last experiment in Table III was measured over a period of two months and the data were plotted by Guggenheim's method; the reaction, however, was not unimolecular over its entire course, but after the time of half completion decreased in rate, the trend amounting to 20%. Experiments were also made in sodium acetate–acetic acid buffer solution, where the reaction was more rapid, and where the increase in rate was roughly proportional to the acetate concentration. The explanation was later discovered to be addition of acetate ion (Reaction III); this reaction will be discussed at some length for epichlorohydrin. From analogy with experiments on ethylene oxide and epichlorohydrin, it is probable that in the phosphate buffer solutions there was also addition.

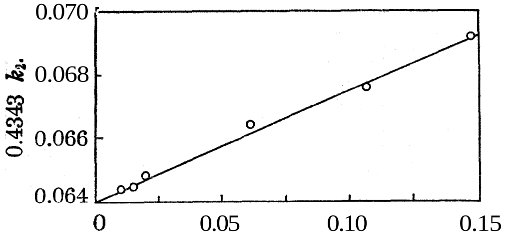


Fig. 4.—Salt effect upon Reaction II. Glycid, c = total salt concentration = M_{HClO_4} + M_{NaClO_4}.

In Table IV are given the results of the experiments in perchloric acid solution. The constant for molar acid, k_2, was obtained as before by subtracting k_1 from the observed velocity constant and dividing the difference by the acid concentration. The correction for the spontaneous reaction is very small as in the case of ethylene oxide. The values of 0.4343 k_2 given in Table IV are shown in Fig. 4 plotted against the total equivalent salt concentration. The salt effect is linear, amounting to 5% in 0.1 N salt solution, as is seen from the equation

Table IV

Effect or Hydrogen Ion upon the Rate or Addition of Water to Glycid. Salt Effect. t = 20°. $0.434\ k_1 = 7.4 \times 10^{-6}$

Molarity, glycid	Molarity, $HClO_4$	Molarity, $NaClO_4$	AR, %	Total equiv. salt concn.	0.4343 k, obs.	0.4343 k_2
0.20	0.01013	0	+1.3	0.010	0.000660	0.0644
.17	.01493	0	+0.6	.015	.000970	.0645
.15	.02023	0	+ .3	.020	.001318	.0648
.14	.01495	0.046	+ .3	.061	.001000	.0664
.14	,01493	.092	+ .5	.107	.001016	.0676
.15	.01495	.132	+ .3	.147	.001042	.0692

$$0.434\ k_2 = 0.0640 + 0.035\ c$$

Experiments were also carried out in solutions of nitric acid, of nitric acid and potassium nitrate, of benzenesulfonic acid, and of benzenesulfonic acid and sodium benzene sulfonate. The results of these experiments are given in Table V.

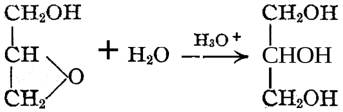
The first column shows the initial acid concentration as calculated from dilution of a standard solution, the second the acid concentration found upon titration of 100 cc. of the residual solution at the end of the experiment. In the first, second and fourth experiments there was undoubted

TABLE V

EXPERIMENTS IN SOLUTIONS OF NITRIC AND OF BENZENE SULFONIC ACID. GLYCID 0.1 M. t = 20°

	Molarity acid, initial	Molarity acid, final	Molarity salt	AR, %	0.434 $k_{obs.}$	0.434 k_2
HNO_3	**0.01538**	**0.01483**	**0**	+3.6	......	....
HNO_3	.01538	.01267	KNO_3, **0.094**	+5.8	......	....
$C_6H_5SO_3H$	.01532	.01518	**0**	+0.3	**0.000976**	**0.0640**
$C_6H_5SO_3H$	.01532	.01419	$C_6H_5SO_3Na$, **0.100**	+1.8	......	....

disappearance of glycid due to Reactions III and IV. Definite velocity constants are recorded for the third experiment only, that in benzenesulfonic acid, without salt. In the other cases it was difficult to draw a representative line through the points obtained by plotting log Av against time as the later points lay well above the line through the earlier. The change in resistance during the experiments, recorded in the fourth column, also substantiate this difficulty. Without any addition of the ions of the acid to glycid during the reaction



$$\begin{matrix} CH_2OH \\ | \\ CH \\ | \quad \rangle O \\ CH_2 \end{matrix} + H_2O \xrightarrow{H_3O^+} \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$$

in perchloric acid solution a slight change in the conductivity of the perchloric acid is expected because of the change in the medium occurring with disappearance of glycid and formation of glycerin. From measurements of the resistance of 0.01000 M perchloric acid in solutions 0.20 M in glycerin and in solutions 0.20 M in glycid, we concluded that an increase of 1% in the resistance is to be expected during the course of the reaction if the initial glycid concentration is 0.20 M. This is qualitatively confirmed by the experiments shown in Table IV.

The increases in resistance in the first, second and fourth experiments of Table V considerably exceed this medium effect.

All these observations tend to confirm the result of the direct titration that acid disappears by the addition Reactions III and IV, these reactions occurring to a greater extent with nitric than with benzene sulfonic acid.

Smith, Wode and Widhe[14] used nitric as well as perchloric acid in measuring Reaction II for ethylene oxide and for epichlorohydrin. They state that the nature of the anion of the catalyzing acid "seems to be of minor importance." Their method of following the reaction was not sufficiently accurate to enable them to detect the complications which we encountered. These complications should, of course, not be neglected when trying to apply the reaction here dealt with for determination of hydrogen-ion concentrations.

4. Results with Epichlorohydrin

The spontaneous addition of water to epichlorohydrin was measured in the same way as the addition of ethylene oxide. Daily readings were taken over a period of a month. The velocity constant, 0.434 k_1, was found to be 2.54 × 10^{-5}, which corresponds to a half time of eight days; Reaction I is therefore approximately three times as fast as in the cases of ethylene oxide and glycid. Two experiments were also carried out in sodium perchlorate solution to determine, if possible, the salt effect upon Reaction I. The results are summarized in Table VI, from which it is evident that there is no detectable salt effect in 0.1 M solution. The solution used in the first experiment was just alkaline to bromthymol blue; the solutions in the second and third experiments were at the change point of bromcresol purple. Hydrogen-ion catalysis was negligible in all experiments. After fourteen days a trace of chloride was detected in the residual portion of the solution used in the first experiment; this was probably due to the hydrolysis of the product of the reaction, $CH_2ClCHOHCH_2OH$, which hydrolyzes much more rapidly than does epichlorohydrin.[17] The reaction showed in no case deviation from unimolecularity.

TABLE VI

THE SPONTANEOUS ADDITION OF WATER TO EPICHLOROHYDRIN. t = 20°

Composition of solution	0.434 $k_1 \times 10^{-5}$
0.10 M Epichlorohydrin in CO_2-free water	2.54
0.10 M Epichlorohydrin in 0.050 M $NaClO_4$	2.57
0.10 M Epichlorohydrin in 0.10 M $NaClO_4$	2.56

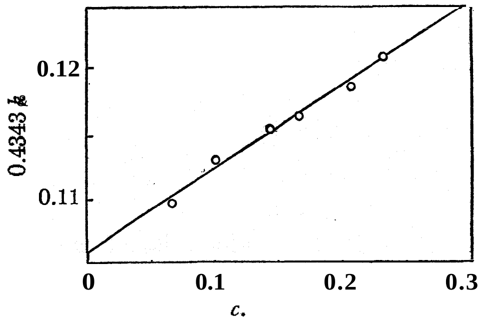


Fig. 5.—salt effect upon reaction II. Epichlorohydrin, c=total salt concentration = $M_{HClO_4} + M_{NaClO_4}$.

The results of the experiments in perchloric acid solution are given in Table VII.

TABLE VII

EFFECT OF HYDROGEN ION UPON THE RATE OR ADDITION OR WATER TO EPICHLOROHYDRIN. SALT EFFECT. t = 20°. 0.434 k_1 = 2.54.10-5

Molarity, epichlorohydrin	Molarity, $HClO_4$	Molarity, $NaClO_4$	ΔR, %	Total equiv. salt concn.	0.4343 k, obs.	0.4343k_2
0.12	0.0673	...	+0.4	0.067	0.000763	0.01097
.14	.1010	...	+ .7	.101	.001167	.01131
.14	.1010	0.042	+ .3	.143	.001192	.01156
.13	.1670	...	+ .5	.167	.001971	.01166
.14	.1009	.106	+ .3	.207	.001224	.01188
.14	.1010	.132	+ .5	.233	.001248	.01211

In Fig. 5, 0.4343 k_2 is plotted against the total equivalent salt concentration.

---

[17] Smith, Z. physik. Chem., 92, 724 (1918).

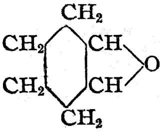
The relationship is evidently linear, k_2 being expressed by the equation

$$0.4343\, k_2 = 0.01059 + 0.0065\, c$$

In 0.1 N salt solution there is, therefore, a 6% salt effect.

5. Results with Cyclohexene Oxide

A few experiments were made with cyclohexene oxide.[18]

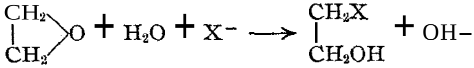


In the presence of perchloric acid this oxide added water very rapidly, the constant for molar acid being $k_2 = 50$.

The constant for the spontaneous reaction is probably small. Dilatometric measurements in acetate and phosphate buffers indicated that the reaction is complicated by Reaction III.

D. Reaction III

Reaction III consists stoichiometrically in an addition of acid to ethylene oxides just as does Reaction IV. Kinetically, however, it is quite different from an addition of acid, the kinetic scheme, as already mentioned, being



$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O + H_2O + X^- \longrightarrow \begin{matrix} CH_2X \\ | \\ CH_2OH \end{matrix} + OH^-$$

where X^- is the anion of the acid. The reaction is therefore independent of the hydrogen-ion concentration. X^- may represent chloride, bromide, iodide, thiocyanate, formate, benzoate, acetate or trimethylacetate ion. From numerous qualitative experiments it would appear that X^- can also represent other anions, the one exception found being perchlorate.

Smith[19] mentions this reaction in the case of chloride ion and glycid in connection with the preparation of β-monochlorohydrin; however, he makes no distinction between this reaction and the direct addition of hydrochloric acid (Reaction IV), which gives the same products as the above reaction in acid solution. As far as we are aware, Reaction III has in the past always been confused with Reaction IV, the direct addition of acid.[20]

Nevertheless, it is Reaction III, not Reaction IV which imparts to the ethylene oxides their conspicuous apparent basicity. These properties are shown not only in the case of "hydrolyzing" chlorides, where the addition of "free acid" may be made responsible for the precipitation of metal hydroxide.[21] They are exhibited in a no less conspicuous manner, for in-

---

[18] "Organic Syntheses," Vol. V, John Wiley and Son, New York, 1925.

[19] Smith, *Z. physik. Chem.*, *94*, 727 (1920).

[20] Cf. Bodfors, *Sammlung chemischer und chemisch-technischer Vorträge*, *26*, 194 (1922).

[21] Cf. Walker, *Ber.*, *34*, 4117 (1901).

stance, in a solution of potassium chloride. Adding to a 0.1 M potassium chloride solution phenolphthalein and a little epichlorohydrin or glycid, one very soon finds the solution pink, the color rapidly deepening to indicate a strongly basic reaction. After titrating the hydroxide formed, the reaction proceeds further.

It is easy to show that the reaction here described is much too rapid to be explained kinetically as an addition of hydrochloric acid. Since the addition of hydrochloric acid is roughly proportional to the concentrations, $c_{H_3O^+}$ and c_{Cl^-}, of the two ions, the reaction should be a million times slower in 0.1 KCl than in 0.1 HCl, if it was kinetically a direct addition of acid. This is very far from being the case. The rate in the salt solution is only fifty times slower than it is in the acid solution. An investigation also showed that the reaction in salt solution was independent of the hydrogen-ion concentration over a considerable range, in conformity with the kinetic scheme of Reaction III.

In order to follow Reaction III it must be isolated from Reactions II and IV. If the hydrogen-ion concentration is kept sufficiently low, Reactions II and IV become negligible and Reaction III may then be studied, account being taken of Reaction I. In addition, the solution must not become too alkaline, for then the reverse reaction may come in. The hydrogen-ion concentration must be kept within the limits 1×10^{-4} and $1 \times 10^{-8.5}$ M. In the study of the addition of the anions of weak acids this is a relatively simple matter, but in the case of the anions of the strong acids it is necessary to make and regulate an artificial buffer solution. On the other hand, the determination of the extent of the reaction is easier in the case of strong acids than in the case of weak.

1. Strong Acids

a. Experimental Method.—When an ethylene oxide disappears by Reaction III, for instance, in a potassium chloride solution, an equivalent amount of potassium hydroxide is set free. In order to study this reaction and to have it proceed undisturbed by other influences, the P_H of the solution should be kept within the limits given above (4 to 8.5) and should also be kept constant as far as possible. The double purpose of measuring the speed titrimetrically and keeping the P_H constant can be sufficiently fulfilled by running continuously into the reacting mixture from a microburet such amounts of strong acid that the solution, to which an indicator is added, always matches in color a constant reference buffer solution containing the same indicator. The reaction then proceeds at the P_H characteristic of the indicator and color chosen, which can be varied from one experiment to another. Its extent is directly recorded by the readings on the buret.

The condition necessary for the application of this principle is, first, that a very small amount of acid should give a sufficient change in the color of the solution in which the corresponding potassium salt is present. For this reason the method is applicable only to salts of strong acids.

In order to avoid too much volume change of the reacting solution, the acid added should be rather concentrated. Since one drop of such a solution would change the P_H far outside the permissible limits, the acid is added from the buret through a very fine capillary ending below the surface of the solution. With continuous stirring by air the color then remained practically uniform throughout the solution.

The details of the experimental procedure were as follows. Two cylindrical vessels of 100-cc. capacity and with capillary tubes sealed to their lower ends were mounted vertically in the thermostat and a white porcelain plate was arranged behind them. A bufier solution with a few drops of indicator was placed in one vessel and the solution of the salt to be studied was placed in the other vessel with an equal amount of indicator. Carbon dioxide-free air was bubbled through the solution and when the solution had come to the temperature of the bath, the oxide was added and the initial time was taken. Meanwhile, a special microburet had been filled with 0.5 M perchloric acid. The tip of the buret was 10 cm. in length and of very narrow bore (approximately 0.12 mm.). The graduated portion of the buret was 20 cm. in length and held 1 cc. of acid. As soon as the oxide was added the tip of the buret, extending through a rubber stopper, was set in the solution, the buret was clamped in place and connected to a device by which the pressure above the acid in the buret could be slightly changed so that the flow of perchloric acid from the buret was just sufficient to keep the solution at the desired hydrogen-ion concentration, as shown by a comparison of the color of the reacting solution with the color of the blank. At convenient times buret readings were taken and the time was recorded. The apparatus was arranged in duplicate and two experiments were carried out at the same time.

b. Calculations.—The velocity constants of each experiment were calculated by the velocity equation

$$-\frac{dc_{Ox.}}{dt} = kc_{Ox.}c_{X^-}$$

where X^- is the anion of the salt solution employed. On integration it gives

$$kt = \frac{1}{0.4343(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

a being the initial concentration of the oxide, b that of the salt and x the concentration of both which has disappeared at the time t. Log $(a-x)/(b-x)$ was plotted against the time in minutes and the best line was drawn through the points. The line has an intercept at the initial time of log a/b. The slope of the line divided by 0.4343 $(a-b)$ gives the velocity constant. As it is not convenient to reproduce these plots, the numerical values are given in Col. 5 of Table VIII, which shows the data of a typical experiment.

In calculating the values of x in this table, the effect of the solution being diluted by the strong acid added has not been taken into account. There

TABLE VIII

ADDITION OF IODIDE ION TO GLYCID. A TYPICAL EXPERIMENT. $t = 20°$

Glycid molarity $= a = 0.0825$. KI molarity $= b = 0.0600$

Time, minutes	Buret reading. Cm.	Cm. × 523 × 10^{-6} = x, molarity of acid added	$\log \frac{a-x}{b-x}$	k_3
0	1.01	......	0.13830	....
10	2.46	0.000758	.13982	0.0156
12	2.79	.000931	.14016	.0159
14	3.08	.001082	.14048	.0159
16	3.37	.001234	.14079	.0159
18	3.69	.001402	.14114	.0161
20	3.94	.001532	.14139	.0159
24	4.51	.001831	.14201	.0158
28	5.04	.002108	.14261	.0158
32	5.62	,002411	.14323	.0157
35	6.19	.002709	.14386	.0163
40	6.83	,003044	.14457	.0161
44	7.33	.003305	.14517	.0160
49	7.98	,003651	.14591	.0159
53	8.50	.003917	.14650	.0158
55	8.77	.004058	.14681	.0159
57	9.03	.004194	.14712	.0158
59	9.30	.004336	.14743	.0158
63	9.80	.004593	.14802	.0158
68	10.40	.004911	.14873	.0157
77	11.50	,005486	.15005	.0156
80	11.87	,005680	.15051	.0156
82	12.10	.005800	.15079	.0156
85	12.50	.006009	,15128	.0156
89	13.00	.006271	.15192	.0156
93	13.45	.006506	.15247	.0156
97	13.91	,006747	.15305	.0155
100	14.29	.006945	.15354	.0156
107	15.10	,007369	.15458	.0155
112	15.67	,007667	.15531	.0157
117	16.27	.007980	.15610	.0155
122	16.75	.008232	.15673	.0154
127	17.33	.008535	,15752	.0154
132	17.90	,008833	,15827	.0154
137	18.41	.009100	.15897	.0154
142	18.90	,009357	.15966	.0154
147	19.45	,009644	.16041	.0154

is also a small correction to be introduced from the disappearance of the oxide by Reaction I, The slight trend shown by the values of k in the fifth column may be explained in that way. Corrections have been introduced for these effectsin Table IX and the following tables.

c. **Results with Glycid.**—The results of a number of experiments with glycid and iodide are summarized in Table IX. The first six experiments show the effect of the acidity. The acidity seems to–have no

TABLE IX

ADDITION OF IODIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KI, molarity	Hydrogen ion. molarity	$NaClO_4$, molarity	k_1
1	0.0819	0.0980	6×10^{-5}		0.0190[a]
2	.0819	.0980	5×10^{-6}		.0161
3	.0819	.0980	6×10^{-7}	...	.0158
4	.0819	.0980	1×10^{-7}	...	.0161
5	.0819	.0980	6×10^{-9}		.0157
6	.0819	.0980	6×10^{-10}		.0140[a]
7	.0825	.0200	1×10^{-7}	...	.0161
8	.0825	.0400	1×10^{-7}	...	.0157
9	.0825	.0600	1×10^{-7}	...	.0157
10	.0825	.0800	1×10^{-7}		.0158
11	.0810	.0200	5×10^{-6}		.0161
12	.0810	.0400	5×10^{-6}	...	.0162
13	.0810	.0600	5×10^{-6}	...	.0159
14	.0918	.0200	1×10^{-7}	...	.0163
15	.0918	.0200	1×10^{-7}	0.176	.0158
16	.1197	.0400	1×10^{-7}	...	.0159
17	.1197	.0400	1×10^{-7}	0.176	.0153

[a] Approximate constants.

influence upon the velocity constant, k_1 within the considerable range of $c_{H_3O^+}$ from 5×10^{-6} to 6×10^{-9}. At higher hydrogen-ion concentration, $c_{H_3O^+} = 6 \times 10^{-5}$, however, the velocity increases, due to Reaction IV, the direct addition of hydrogen iodide. It is here no longer possible to obtain a good velocity constant, because the adjustment of the PH by means of the color of the indicator is not accurate enough when the hydrogen ion enters into the reaction to a considerable extent. At a hydrogen-ion concentration of 6×10^{-10} *M* the calculated values of k decrease as the reaction proceeds; the reaction is probably no longer going to completion. This effect, however, was not investigated further.

Experiments 7–13 were carried out to study the effect of the concentration of the iodide. The rate is very nearly proportional to this concentration. As indicated by the results of these experiments and Expts. 14–17 in which sodium perchlorate was added, there seems to be a small negative salt effect.

The addition of bromide and of chloride is much slower than that of iodide and in the case of the chloride it is necessary to work at higher salt concentrations. As was found with the iodide the reaction is independent of the hydrogen-ion concentration and a negative salt effect is indicated. The results are summarized in Tables X and XI.

It was also found that thiocyanate adds to glycid at a rate comparable to that of iodide.

As is shown in Table XII, the rate was no longer found to be independent of the hydrogen-ion concentration at a hydrogen-ion concentration of

TABLE X

ADDITION OF BROMIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KBr, molarity	Hydrogen ion, molarity	$k_3 \times 10^5$	
1	0.0857	0.0990	2×10^{-4}	215"	
2	.0842	.0990	6×10^{-5}	133"	
3	.0911	.0990	6×10^{-7}	98.6	100.7
4	.0886	.0990	5×10^{-6}	102.9	
5	.0911	.0990	1×10^{-7}	99.9	
6	.0905	.1000	1×10^{-7}	101.3	
7	.0886	.0990	6×10^{-9}	92.2"	
8	.0857	.0990	6×10^{-10}	90.0[a]	
9	.0842	.0990	1×10^{-7}	97.2	
10	.0905	.2000	1×10^{-7}	92.0	

[a] Approximate constants.

TABLE XI

ADDITION OF CHLORIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KCl, molarity	Hydrogen ion, molarity	$k_3 \times 10^6$
1	0.2700	0.1000	1×10^{-7}	149
2	.2469	.2000	1×10^{-7}	142
3	.2117	.5000	1×10^{-7}	139
4	.2325	,8000	5×10^{-6}	130
5	.2330	.8000	1×10^{-7}	126

TABLE XII

ADDITION OF THIOCYANATE TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KCNS, molarity	Hydrogen ion, molarity	$k_3 \times 10^5$
1	0.08081	0.2000	4×10^{-4}	840[a]
2	.08273	.2000	6×10^{-5}	782
3	.08456	.2000	6×10^{-7}	744
4	.08273	.2000	6×10^{-7}	746
5	.08273	.2000	1×10^{-7}	792
6	.08456	.2000	6×10^{-9}	795
7	,08273	.2000	6×10^{-10}	785
8	.08176	.2000	6×10^{-9}	758
9	.08081	.2000	1×10^{-7}	744
10	.1670	.1000	1×10^{-7}	781

[a] Approximate constants.

4×10^{-4} M. Thiocyanic acid, therefore, adds to glycid as do the halogen acids.

The salt effect $(1/k_0)(dk/dc)$ in the experiments with chloride, bromide and iodide is on an average -0.30 (k_0 is the velocity constant at zero salt concentration). Taking this to be true also for the thiocyanate, we find that the constants of the four reactions can be represented by

$$k_{\mathrm{Cl}^-} = 150 \times (1 - 0.30c) \times 10^{-6}$$
$$k_{\mathrm{Br}^-} = 103 \times (1 - 0.30\sim) \times 10^{-5}$$
$$k_{\mathrm{Th}^-} = 79 \times (1 - 0.30c) \times 10^{-4}$$
$$k_{\mathrm{I}^-} = 162 \times (1 - 0.30c) \times 10^{-4}$$

d. Results with **Epichlorohydrin.**—The results with epichlorohydrin are quite parallel to those with glycid. The rate of addition is independent of the hydrogen-ion concentration over a considerable range and is proportional to the concentration of the reacting ion. In all cases the reaction is approximately four times as fast as the corresponding reaction with glycid. In studying the addition of iodide to epichlorohydrin, owing to the speed of this reaction, we were able to work at iodide concentrations less than 0.01 M and to follow the reaction practically to completion. In order to avoid the various corrections being greatly magnified with the extent of the reaction, we used, however, only the first part of the reaction, where these corrections are small. The results are given in Table XIII. In the fifth experiment of Table XIII the epichlorohydrin concentration was low and the iodide concentration high, so that the major part of the correction was for the spontaneous reaction.

TABLE XIII

ADDITION OF IODIDE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KI, molarity	Hydrogen ion, molarity	$k_3 \times 104$
1	0.2466	0.0100	5×10^{-6}	595
2	.2378	.00665	5×10^{-6}	610
3	.2970	.00810	5×10^{-6}	620
4	.2480	.00669	1×10^{-7}	587
5	.0119	.2100	1×10^{-7}	584
6	.0813	,02169	1×10^{-7}	604
7	.0813	.02500	1×10^{-7}	609
8	.0650	.02500	1×10^{-7}	584
9	.0650	.02255	1×10^{-7}	581

The experiments on the addition of bromide, chloride and thiocyanate ion to epichlorohydrin are summarized in Tables XIV, XV and XVI. In Tables XIV and XV, where experiments at widely varying salt concentrations are recorded, the figures show the presence of a negative salt effect as in the case of glycid, but somewhat smaller (0.2 instead of 0.3). If the same salt effect is assumed to exist in all four salt solutions, which

TABLE XIV

ADDITION OF BROMIDE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KBr, molarity	Hydrogen ion, molarity	$k_3 \times 10^5$
1	0.0836	0.1000	1×10^{-7}	359
2	.0836	.1000	6×10^{-7}	361
3	.C660	.2000	1×10^{-7}	345
4	.0660	.2000	6×10^{-7}	356
5	.0688	.5000	1×10^{-7}	338
6	.C688	.5000	1×10^{-7}	335
7	.1060	1.000	1×10^{-7}	282

TABLE XV

ADDITION OF CHLORIDE ION TO EPICHLOROHYDRIN. t = 20°

Expt.	Epichlorohydrin, molarity	KCl, molarity	Hydrogen ion, molarity	$k_3 \times 10^6$
1	0.0672	0.2000	1×10^{-7}	677
2	.0672	.2000	1×10^{-7}	667
3	.0868	.3000	1×10^{-7}	675
4	.0868	.4000	1×10^{-7}	633
5	.0776	.4000	1×10^{-7}	662
6	.0776	.5000	1×10^{-7}	650
7	.0867	.6000	1×10^{-7}	619
8	.1130	.8000	1×10^{-7}	569

TABLE XVI

ADDITION OR THIOCYANATE ION TO EPICHLOROHYDRIN. t = 20°

Expt.	Epichlorohydrin, molarity	KCNS, molarity	Hydrogen ion, molarity	$k_3 \times 10^4$
1	0.0979	0.02000	1×10^{-7}	370
2	.0898	.04000	1×10^{-7}	368
3	.0228	.1000	1×10^{-7}	371

is of course only approximately true, the constants can be given by the following equations

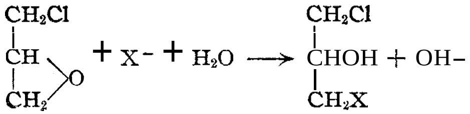
$$k_{\mathrm{Cl}^-} = 69 \times (1 - 0.2c) \times 10^{-5}$$
$$k_{\mathrm{Br}^-} = 37 \times (1 - 0.2c) \times 10^{-4}$$
$$k_{\mathrm{Th}^-} = 38 \times (1 - 0.2c) \times 10^{-3}$$
$$k_{\mathrm{I}^-} = 60 \times (1 - 0.2c) \times 10^{-3}$$

Ethylene oxide is so volatile that it is impossible to obtain quantitative results using this method of following the reaction; qualitative experiments, however, indicate that the rates are approximately the same as with glycid.

2. Weak Acids

In a mixture of acetic acid and acetate ions and in similar buffers the weak acid is added to epichlorohydrin by Reaction III. As the reaction proceeds, the PH of the buffer varies only slightly in the first part of the reaction. The device of artificially maintaining a certain value of the hydrogen-ion concentration, as in the case of strong acids just described, was therefore not necessary. For the same reason, however, also the method used there for following the reaction was inapplicable.

The rate of addition of the anion was determined by titration of the acid from time to time in samples of the reacting solution. Since addition of the anion results in the formation of the hydroxyl ion and consequent neutralization of the acid of the buffer



$$\mathrm{OH^- + HX \longrightarrow H_2O + X^-}$$

the concentration of the anion remains constant. The epichlorohydrin in such a buffer solution disappears by two paths, by Reaction I, the spontaneous, and by Reaction III above. Since the duration of an experiment here was much longer than in the case of strong acids, Reaction I becomes predominant and must be eliminated in order to calculate the constant of Reaction III.

Representing by a the initial concentration of epichlorohydrin, by x the concentration of monochlorohydrin formed at time t and by y the concentration of addition compound formed by Reaction III, one has

$$\frac{dx}{dt} = k_1(a - x - y) \tag{1}$$

$$\frac{dy}{dt} = k'(a - x - y) \tag{2}$$

where k_1 is known (0.434 $k_1 = 2.54 \times 10^{-5}$, *cf.* p. 438) and $k' = k_3c$, c being the concentration of the anion. In order to find k' one divides Equation 1 by Equation 2 and integrates

$$\frac{x}{y} = \frac{k_1}{k'} \text{ or } x + y = y \times \frac{k_1 + k'}{k'}$$

Substituting this value for $x + y$ in (2) and integrating, one has

$$\ln \frac{a}{a - \dfrac{k_1 + k'}{k'}y} = (kt + k')t \tag{3}$$

by which k' is determined, since y equals the concentration of acid which has disappeared, which has been found by the titration. In order to solve for k', we chose a number of arbitrary values of k', plotted the value of the ln of Equation 3 against k', and $t\,(k_1 + k')$ against k', the intersection of the curve representing the logarithmic expression and the line representing $(k_1 + k')\,t$ gave the value of k' satisfying Equation 3. In estimating the acetic acid, enough standard sodium hydroxide solution, 0.02 M, was added to neutralize nine-tenths of the acid; carbon dioxide-free air was bubbled through the solution for twenty minutes and the solution was then titrated to the appearance of the pink color of phenolphthalein. Table XVII shows a typical experiment.

The fourth column contains the arbitrarily chosen values of k', the fifth the corresponding values of the logarithmic expression, and the sixth the corresponding values of $t\,(k_1 + k')$. The seventh column gives the value of k' at the intersection of the curve and the line obtained when $2.30 \log \dfrac{a}{a - y(k_1 + k')/k'}$ and $(k_1 + k')\,t$, respectively, are plotted against k'. The velocity constant, k_3, is obtained by dividing k' by the acetate-ion concentration. Experiments were carried out with acetic, formic, benzoic and trimethylacetic acids. The results of all of the experiments are collected in Table XVIII.

TABLE XVII

ADDITION OF ACETATE ION TO EPICHLOROHYDRIN. t = 20°. A TYPICAL EXPERIMENT NaAc, 0.100 M. Initial Concn. of Epichlorohydrin, 0.1000 M

Time, minutes	Concn. HAc, molarity	Y	$k' \times 10^5$ assumed	$2.30 \times \log \frac{a}{a - Y\frac{k_1 + k'}{k}}$	$t(k_1 + k')$	$k' \times 10^5$ selected
..	0.02028	.....	....	....	....	..
1140	.01642	0.00386	3.00, 3.50, 3.60, 4.00	0.121, 0.109, 0.106, 0.100	0.101, 0.107, 0.108, 0.112	3.56
2685	.01148	.00880	3.30, 3.50, 3.70, 4.00	0.280, 0.268, 0.257, 0.243	0.245, 0.251 0.256, 0.264	3.71
4000	.00793	.01235	3.40, 3.70, 4.00	0.409, 0.383, 0.365	0.370, 0.382 0.394	3.71
5450	.00460	.01568	3.40, 3.70, 4.00	0.555, 0.518, 0.488	0.504, 0.520, 0.536	3.68
6890	.00179	.01849	3.40, 3.70, 4.00	0.698, 0.648, 0.607	0.637, 0.657, 0.678	3.66
					Average,	3.66

TABLE XVIII

ADDITION OF THE ANIONS OF CARBOXYLIC ACIDS TO EPICHLOROHYDRIN. t = 20°

Acid	Dissoc. const.	Initial concn. of acid, molarity	Concn. of Na salt, molarity	$k \times 10^5$	$k_3 \times 10^4$
Formic	2.1×10^{-4}	0.0203	0.200	5.57	2.79
		.0103	.200	5.83	2.91
		.0103	.100	2.88	2.88
				Average,	2 86
Benzoic	0.6×10^{-4}	.0141	.149	4.59	3.08
		.0193	.149	4.59	3.08
		.0096	.099	3.02	3.05
				Average,	3.07
Acetic	0.18×10^{-4}	.0203	.100	3.66	3.66
		.0104	.100	3.70	3.70
		.0202	.050	1.86	3.72
		.0100	.050	1.82	3.64
		.0200	.020	7.35	3.68
		.0100	.020	7.55	3.78
				Average,	3.70
Trimethylacetic	0.10×10^{-4}	.0146	.050	2.50	5.00
		.0179	.025	1.26	5.04
		.0150	.025	1.25	5.00
				Average,	5.01

The experiments in formate–formic acid buffer solution are within themselves less accurate than the rest. It was found to be impossible to titrate the formic acid using phenolphthalein as indicator; in the slightly alkaline solution formic acid was regenerated and no end-point could be obtained. The method finally adopted was to add enough sodium hydroxide solution to neutralize nine-tenths of the formic acid, air for fifteen minutes and to remove carbon dioxide and titrate rapidly to the change-point of bromthymol blue,

From Table XVIII it is evident that the rate of reaction is proportional to the anion concentration and independent of the concentration of the acid and of the hydrogen ion over the range studied. In other words, it is actually Reaction III which is responsible for the addition of weak acid. It is also evident that any salt effect amounts to less than 2% in 0.1 N solution.

E. Reaction IV

As mentioned already in the Introduction, the primary purpose of the present work was to study Reaction IV, the direct addition of strong acid to ethylene oxides, from the stand-point of the modern theory of the velocity of ionic reactons.

Only little is known of the kinetics of this addition reaction. Bodfors[20] states that the reaction is probably more rapid with hydrobromic than with hydrochloric acid. With hydriodic acid a simultaneous reduction of the oxide is known to occur.

The addition of hydrochloric acid to epichlorohydrin has recently been found by Smith, Wode and Widhe[14] to be a reaction of the third order. These authors followed the reaction by an analytical method; they worked at comparatively high acid concentrations (0.07–0.13 *M*), they did not recognize the presence of Reactions I and III, and from their results the salt effect upon Reaction IV cannot be determined.

A number of preliminary experiments were carried out in order to determine under what conditions Reaction IV might best be studied. In these experiments the reaction was followed by measurement of the diminution in the conductivity of the solution with addition of acid, the oxide being always present in great excess. An approximate velocity constant was calculated from the equation

$$-\frac{\mathrm{d}c_{\text{Acid}}}{\mathrm{d}t} = kc_{\text{Oxide}}c^2_{\text{Acid}}$$

or

$$\frac{\mathrm{d}\left(\frac{1}{c_{\text{Acid}}}\right)}{\mathrm{d}t} = kc_{\text{Oxide}}$$

by plotting the reciprocal of the acid concentration against time and dividing the slope of the best line through the early points by the oxide concentration. The results of these preliminary experiments are given in Table XIX.

It appears from these figures that the addition of hydrobromic acid is four or five times as rapid as the addition of hydrochloric acid in both the ethylene oxide and epichlorohydrin reaction and also that the reaction with ethylene oxide is about four times as rapid as the reaction with

TABLE XIX

PRELIMINARY EXPERIMENTS ON REACTION IV

Oxide	Init. concn., molarity	Acid	Init. concn., molarity	Temp., °C.	*k*
Ethylene oxide	0.12	HBr	0.010	25	8.7
Ethylene oxide	.14	HCl	.010	25	2.2
Ethylene oxide	0.13– .27	HBr	.010	18	4.2[a]
Glycid	.14	HBr	.010	20	3.3
Epichlorohydrin	.15	HBr	.010	20	1.3
Epichlorohydrin	.15	HCl	.010	20	0.27

[a] The average of the values from four experiments.

epichlorohydrin. For the accurate measurements we decided upon the hydrobromic acid–glycid reaction as probably the most suitable.

1. Description of Experimental Part

The disappearance of hydrobromic acid in the glycid solution was measured by the conductivity of the solution in the conductivity cell shown in Fig. 1. The relation between conductivity and concentration of pure aqueous hydrobromic acid solutions was first determined in the same cell. From this relationship the concentration in the solutions in which the addition took place was calculated on two assumptions; first, that the medium effect of glycid upon the conductivity of hydrobromic acid was the same as the medium effect upon the conductivity of perchloric acid, for which an increase of 1.2% in resistance was found to correspond to a concentration of 0.10 M glycid; and, second, that the medium effect of the glycid, glycerin and bromohydrin present in the solution after the start was the same as the initial medium effect of the glycid. This is certainly not exactly true but may be taken as a sufficient approximation.

The cell constant was obtained by measurement of the conductivity of a *N*/50 potassium chloride solution; the value of Kohlrausch, Holborn and Diesselhorst,[22] was applied for the specific conductivity of *N*/50 potassium chloride solution at 20°.

The acid used was made from Kahlbaum's 25% hydrobromic acid, which was distilled in an all-glass apparatus; the second half of the distillate was redistilled and the middle portion of the second distillate (passing over under a pressure of 764 mm. and containing 47.8% of hydrogen bromide) was taken for the experiments. Solutions ranging from 0.06 to 0.001 M were measured. Excepting the original solution, 0.06173 M, each solution of hydrobromic acid was prepared at room temperature by dilution to one liter of 500 cc. of the preceding solution. No solvent correction was made; it may be mentioned, however, that the specific con-

---

[22] Landolt, Bornstein, Roth, Scheel, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1098.

ductivity of the water used was 2.4 × 10^{-6} reciprocal ohms. The molecular conductivities are given in Table XX and are shown in Fig. **6** plotted against the square roots of the hydrobromic acid concentration.

Table XX

Molecular Conductivity of Hydrobromic Acid. $t = 20°$

HBr, molarity	Molecular conductivity	HBr, molarity	Molecular conductivity
0.06173	366.8	0.003858	386.4
.03087	374.2	.001929	388.9
.01543	379.6	.000965	389.9
.007717	383.4		

The experimental procedure for determining the rate of addition was the following. A glycid solution was placed in Cell A and allowed to come to the temperature of the thermostat, after which a certain volume was removed with a pipet and an equal volume of hydrobromic acid solution was added. Carbon dioxide-free air was bubbled through the solution in order to mix it and readings of the resistance of the solution were then made at convenient intervals.

The values of the molal conductivity shown in Table XX were plotted against the logarithm of the corresponding resistances. By referring the logarithm of the resistance of the reacting solution corrected for the medium effect, to this graph, the corrected molal conductivity was obtained and from this again the concentration of the hydrobromic acid in the reacting solution was calculated.

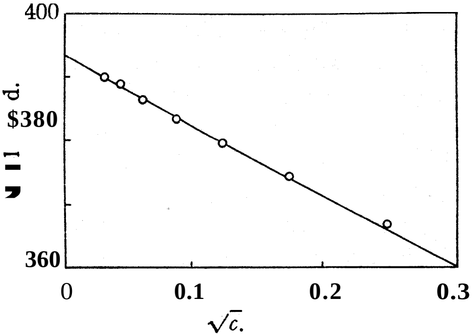


Fig. 6.—Molal conductivity of hydrobromic acid, c = molality of HBr.

2. Calculations

As already pointed out, in an aqueous solution of hydrobromic acid and glycid four reactions occur. Letting x be the concentration of glycid and y the concentration of hydrobromic acid in moles per liter, we may express the kinetic equations of these reactions as follows:

(Reaction I) **Glycid + $H_2O \longrightarrow$ Glycerin**

$$-\left(\frac{dx}{dt}\right)_1 = k_1x \qquad (1)$$

(Reaction II) **Glycid + $H_2O \xrightarrow{H_3O^+}$ Glycerin**

$$-\left(\frac{dx}{dt}\right)_2 = k_2xy = (k_2' + k_2''y)xy \qquad (2)$$

(Reaction III) Glycid + Br^- + H_2O ⟶ Bromohydrin + OH^-

$$-\left(\frac{dx}{dt}\right)_3 = k_3xy; \quad -\left(\frac{dy}{dt}\right)_3 = k_3xy \qquad (3,\ a \text{ and } b)$$

(Reaction IV) Glycid + Br^- + H_3O^+ ⟶ Bromohydrin + H_2O

$$-\left(\frac{dx}{dt}\right)_4 = -\left(\frac{dy}{dt}\right)_4 = k_4xy^2f^2 \qquad (4,\ a \text{ and } b)$$

In setting up these equations the salt effect upon Reaction I and III, which are insignificant, have been neglected. In Reaction II the salt effect has been taken care of by the member k''_2y. The equation developed for Reaction IV is identical with Equation 1 on p. 429 and is the relation to be tested; f indicates the activity coefficient of a univalent ion, for which the equation[23]

$$-\log f = 0.5\sqrt{c} - 0.5c \qquad (5)$$

is supposed to hold.

According to the theoretical Equation 4, the direct addition of hydrobromic acid to glycid is no simple third order reaction. Calculating the reaction constant, k_4f^2, under the presupposition of a simple third-order reaction, we shall expect it to increase steadily during an experiment due to the increase in f as the reaction proceeds.

The constants k_1, k'_2, k''_2 and k_3 are all known from the preceding sections, namely, $k_1 = 2.30 \times 7.4 \times 10^{-6}$; $k'_2 = 2.30 \times 0.0640$; $k''_2 = 2.30 \times 0.035$; $k_3 = 0.00100$. The problem is to decide whether the experiments can be satisfied by a constant value of k_4 and to find its value.

The rate of disappearance of glycid from Equation 1 to 4 is

$$-\frac{dx}{dt} = k_1x + k'_2xy + k''_2xy^2 + k_3xy + k_4xy^2f^2$$

and the rate of disappearance of acid

$$-\frac{dy}{dt} = k_3xy + k_4xy^2f^2$$

We wish to integrate these equations in such a way that from an observed relationship between y and t we are in a position to determine the unknown quantity, k_4. This problem can be solved in a way which has been pointed out by Mr. B. Jessen. We are much indebted to him for this assistance and also for his carrying out a great part of the rather lengthy numerical calculations.

Let

$$k_1 + k'_2y + k''_2y^2 = g \qquad (6)$$

a known function of y, and

$$k_3y + k_4y^2f^2 = h \qquad (7)$$

an unknown function of y. The differential equations then become

$$-\frac{dx}{dt} = (g + h)x \qquad (8)$$

---

[23] Cf. Bronsted, *Trans. Faraday Soc.*, *23*, *416* (1927).

and

$$-\frac{dy}{dt} = hx \tag{9}$$

Subtracting, we have

$$-\frac{d(x-y)}{dt} = gx$$

and letting $x - y = X$

$$-\frac{dX}{dt} = gX + gy$$

Since g and gy are known functions of t, the above equation in X is linear and of the first degree in X and dX/dt can be integrated; the integrated form is

$$X = \frac{1}{S}\left[X_0 - \int_0^t gyS\,dt\right] \tag{10}$$

where S is given by

$$\ln S = \int_0^t g\,dt$$

We now have x or X + y as a function of t, and from the slope of the curve obtained by plotting y against t, the value of the function h may be found at any time. From Equation 2 we have

$$k_4f^2 = \frac{h - k_3y}{y^2} \tag{11}$$

the value of which is now determined by inserting for y and h their proper values. The constancy of k_4 thus determined will furnish a test of the correctness of the equation used for describing Reaction IV.

From Table XXI, in which the results of a typical experiment are given, the procedure of the calculations appears clearly.

TABLE XXI

THE ADDITION OF HYDROBROMIC ACID TO GLYCID. $t = 20°$

Time, minutes	$y \times 10^5$	$-\frac{dy}{dt} \times 10^5$	$g \times 10^5$	S	x	k_4f^2	$\log k_4 + 2 \log f$
0	991	...	148	1.00	0.1456	..	...
10	945	4.23	141	1.02	.1432	3.20	0.505
20	902	3.84	137	1.03	.1406	3.24	.511
30	866	3.49	129	1.04	.1385	3.24	.511
40	832	3.16	124	1.06	.1364	3.23	.509
50	802	2.88	120	1.07	.1345	3.24	.510
60	774	2.65	116	1.08	.1326	3.20	.505
70	749	2.45	112	1.09	.1308	3.21	.506
80	725	2.27	109	1.11	.1292	3.21	.506
90	702	2.12	105	1.12	.1275	3.24	.510
100	682	1.99	102	1.13	.1261	3.18	.503
110	662	1.86	99.2	1.14	.1246	3.26	.513
120	645	1.76	96.6	1.15	.1232	3.28	.516
130	627	1.66	94.0	1.16	.1219	3.31	.520
140	611	1.57	91.6	1.17	.1206	3.33	.522
150	595	1.49	89.3	1.18	.1194	3.36	.526

TABLE XXI (*Concluded*)

Time, minutes	$y \times 10^5$	$-\frac{dy}{dt} \times 10^5$	$g \times 10^5$	S	x	k_4f^2	$\log k_4 + 2 \log f$
160	581	1.41	87.2	1.20	0.1181	3.37	0.528
170	567	1.34	85.1	1.21	.1171	3.38	.530
180	554	1.27	83.2	1.22	.1158	3.38	.530
200	530	1.15	79.6	1.24	.1138	3.42	.534
220	508	1.04	76.5	1.26	.1118	3.41	.533
240	488	0.945	73.5	1.27	.1100	3.40	.532
260	470	.860	70.9	1.29	.1082	3.38	.530
280	454	.799	68.4	1.31	.1065	3.43	.535
300	438	.725	66.2	1.33	.1050	3.37	.528
320	424	.671	64.1	1.35	.1034	3.37	.528
340	411	.621	62.2	1.36	.1020	3.36	.526
360	399	.584	60.4	1.38	.1006	3.38	.530
380	388	.543	58.8	1.40	.0994	3.37	.528
400	377	.512	57.2	1.41	.0981	3.41	.533
1320	181	.0923	28.3	2.02	.0670	3.65	.562
1380	175	.0852	27.4	2.05	.0658	3.65	.562
1440	170	.0790	26.7	2.09	.0647	3.64	.561
1500	165	.0736	26.0	2.12	.0637	3.64	.561
1560	161	.0688	25.4	2.15	.0627	3.61	.558
1620	157	.0647	24.8	2.18	.0617	3.61	.558
1680	154	.0610	24.3	2.22	.0608	3 61	.558
1740	150	.0582	23.8	2.25	.0598	3.66	.564

The initial values of glycid and hydrobromic acid (x_0 and y_0) were 0.1456 and 0.00991, respectively. The values of the concentration of hydrobromic acid (Col. 2) at the time, t (Col. 1), are smoothed values taken from a graph in which y, determined by the conductivity method as described (p. 451), was plotted against t. The fourth column contains the function g or $k_1 + k_2'y + k_2''y^2$ calculated from the values of the constants given above. The fifth contains S, i. e., the antilogarithm of the integral 0.4343 $\int_0^t$ gdt obtained by graphic integration. The sixth column contains the glycid concentration x, which is equal to

$$\frac{1}{S}\left[X_0 - \int_0^t gySdt\right] + y$$

Here again the integral was evaluated graphically. The seventh column records k_4f^2, the classical velocity constant, calculated by Equation 11; the eighth, its logarithm.

3. Results

In Fig. 7 the velocity constant k_4f^2 from Table XXI is plotted against hydrobromic acid concentration and in Fig. 8 the logarithm of the same velocity constant is plotted against the square root of the acid concentration. From the first plot the increasing change in the constant with decreasing acid concentration predicted by the theory appears. The second plot gives a simple quantitative picture of this change. Since the activity coefficient f is given by Equation 5, the limiting slope for small concentrations in the plot, Fig. 8, should be

$$\frac{d \log (k_4 f^2)}{d\sqrt{c}} = -1$$

The straight line in Fig. 8 is drawn with this slope, to which the measurements are seen actually to conform very well.

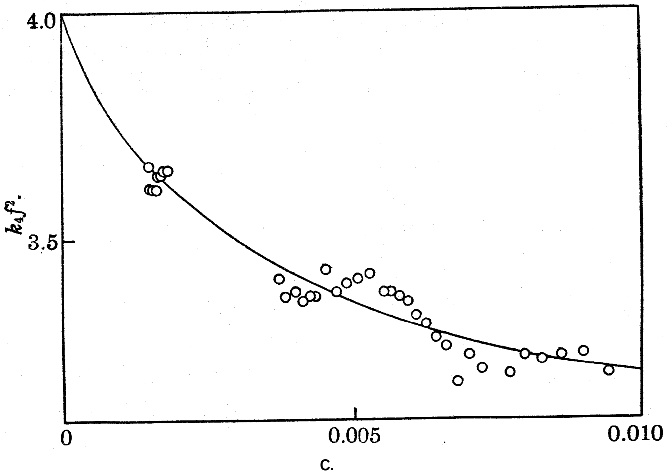


Fig. 7.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

In addition to the one experiment here described, five other experiments were performed in which the initial glycid concentration ranged from

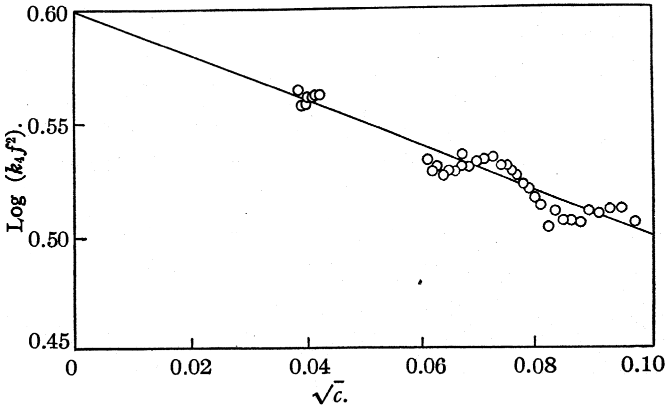


Fig. 8.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

0.045 to 0.15 M, and the initial hydrobromic acid concentration from 0.0067 to 0,041 M. The series of velocity constants $k_4 f^2$ obtained for all the experiments in quite the same way as above were plotted against the hydrobromic acid concentrations, as is done for a single experiment in Fig. 7, and through the band of points a representative curve was drawn. In Table XXII are shown the velocity constants taken from this curve and corresponding to specified hydrobromic acid concentrations.

TABLE XXII

THE VELOCITY OF REACTION IV

Glycid + Hydrobromic Acid ⟶ Bromohydrin

HBr concn., molarity	Obs. velocity constant (k_4f^2)	**log** k_4 + 2 logf	**HBr** concn., **molarity**	Obs. velocity constant (k_4f^2)	log k_4 + 2 **log**
0.00100	3.72	0.571	0.0100	3.17	0.501
.00200	3.59	.555	.0125	3.10	.491
.00300	3 47	.540	.0150	3.04	.483
.00400	3.41	.533	.0175	2.99	.476
.00500	3.35	.525	.0200	2.95	.470
.00600	3.30	.519	.0250	2.87	.458
.00700	3.27	.515	.0300	2.81	.499
.00800	3.23	.509	.0350	2.75	.439
.00900	3.20	.505	.0400	2.69	.430

The logarithms of the velocity constants, k_4f^2, given in the third column of Table XXII are plotted in Fig. 9 against the square roots of the acid concentrations. The dotted line in the graph indicates the theoretical limiting slope. The full curve is drawn to satisfy the equation

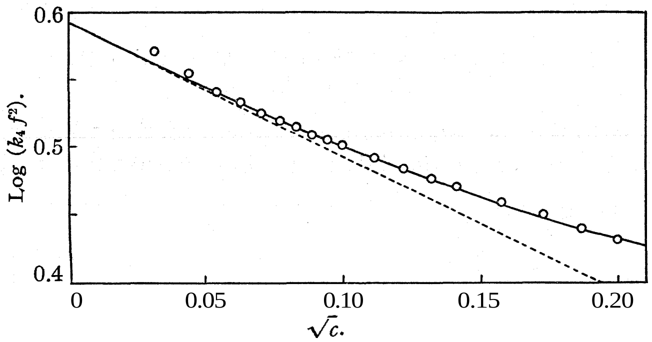


Fig. 9.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

$$\log (k_4f^2) = 0.592 + \sqrt{c} + c$$

which takes into account the deviations from the limiting slope at higher acid concentrations.

Except for the two points in the most dilute region, where the experimental error is greatest, the experimental points are obviously located very closely on this curve. This means that the experimental points satisfy the two equations $\log k_4 = 0.592$ and $2 \log f = \sqrt{c} + c$, the latter of which is identical with Equation 5. In other words, since f is known to follow Equation 5, the experiments have shown k_4 to be a constant independent of the acid concentration.

In spite of the interference of three other processes, it has thus been possible to show that the direct addition of a strong acid to glycid follows the requirement of the modern theory of velocity of ionic reactions.

F. Discussion

From the results stated in the previous sections it is evident that the "basicity" of ethylene oxides is a property which is exhibited in solutions of these substances only under certain conditions and is not at all inherent in the oxide molecules as in the case of true bases. The oxide molecules are unable—at least to an extent detectable in the ordinary experiment—to exert the basic function which consists in the simple addition of protons. If the oxide molecule takes up a proton it invariably at the same time adds also an anion, and if no suitable anion is available it remains unchanged.

The simultaneous addition of a proton and an anion amounts to the addition of a hydrogen compound. If this hydrogen compound is an acid, for instance, hydrochloric acid, the reaction makes the acidity of the solution decrease and the oxide seems to be basic. The tendency to add an acid may be so strong that the reaction proceeds rapidly even in an aqueous solution which is already "neutral" or "basic" (for instance in potassium iodide). The hydrogen compound in question, however, need not be of acid character. The ethylene oxides, for instance, add basic hydrogen compounds, and the occurrence of this reaction in water solution may cause an increase in acidity. The conclusion on the basis of such phenomena that ethylene oxide is an acid would be justified to the same extent as the conclusion of its being a base on the basis of its adding hydrogen chloride.

The truth, of course, is this, that the ethylene oxides do not possess the character of bases. Applying to them the term of "pseudo-bases" would not even be an adequate description of their nature. Their apparent basicity (and acidity) simply originate in their tendency to combine directly with, and thus to remove from the solution, a multitude of substances, whereby, according to the nature of the substance removed and formed, the acidity of the solution may increase or decrease. Since the reactions by which acids are taken up are the more numerous and conspicuous, the idea generally adopted of a special basicity of these oxides becomes intelligible.

As to the kinetic mechanism by which the basicity in a solution is produced, it has been shown above that two Reactions (III and IV) are effective. While Reaction IV, or the direct addition of acids, takes place in the case of the halide acids, Reaction III seems to occur more generally for both weak and strong acids. Perchloric acid is the only one for which no indication of addition has been found either by Reaction III or IV. It is Reaction III which is essentially responsible for the phenomenon of "basicity" observed in solutions of ethylene oxides under ordinary conditions.

The study of the different reactions in which the ethylene oxides take part has also contributed to the verification of the general theory of reaction velocity.[3,4] For Reaction II, which takes place between the oxide molecule and the hydrogen ion, this theory requires a linear salt effect which has actually been found (Tables II, IV and VII) in the hydrogen-ion catalysis of all three oxides investigated. It is in conformity with this theory that the concentration of the hydrogen ion in these reactions is the factor by which the reaction is mainly controlled. Essentially the same laws hold good in the case of Reaction III. Reaction IV, on the other hand, is a reaction between ions of opposite sign, and should theoretically be characterized by a negative exponential salt effect. As shown above (Section P, 3) this is actually found and the salt effect demonstrated corresponds closely to the requirements of the theory.

In order to compare the velocities of the various reactions, the constants are collected in tables below. Table XXIII contains the unimolecular constants for Reactions I and II for the three oxides investigated.

TABLE XXIII

$t = 20°$

	k_1 (Spont. react.)	k_2 (Hydrogen-ion catal.)
Ethylene oxide	2.16×10^{-5}	$0.320 + 0.28c$
Glycid	1.70×10^{-5}	$0.147 + 0.081c$
Epichlorohydrin	5.84×10^{-5}	$0.0244 + 0.0150c$

The constants seem to depend upon the substance in an individual manner. While in passing from ethylene oxide to glycid both constants decrease somewhat, there is a considerable increase in k_1 and a considerable decrease in k_2 passing from these oxides to epichlorohydrin. The ratios glycid/epichlorohydrin are

$$\left(\frac{k_{\text{Gl}}}{k_{\text{Ep}}}\right)_1 = 0.29 \qquad \left(\frac{k_{\text{Gl}}}{k_{\text{Ep}}}\right)_2 = 6.0$$

The constants for Reaction III are given in Table XXIV.

TABLE XXIV

k_3 AT ZERO SALT CONCENTRATION. $t = 20°$

Ion reacting	Glycid	Epichlorohydrin	$(k_{\text{Gl}}/k_{\text{Ep}})_0$
I^-	1.62×10^{-2}	6.0×10^{-2}	0.27
Th^-	7.9×10^{-3}	3.8×10^{-2}	.21
Br^-	1.03×10^{-3}	3.7×10^{-3}	.28
Cl^-	1.50×10^{-4}	6.9×10^{-4}	.22
Formate	....	2.8×10^{-4}	
Benzoate	....	3.1×10^{-4}	
Acetate	....	3.7×10^{-4}	
Trimethylacetate	....	5.0×10^{-4}	

In this table the anions—except for Th^-, the thiocyanate ion, the strength of which is unknown—are arranged according to basic strength. This factor, however, does not seem to control the reactions, since in the case of the halide ions the velocity increases with decreasing strength, while the converse is true for the anions of the four organic acids. In the cases of the very weak base Cl^- and the relatively strong trimethylacetate ion, the rates are practically the same. As shown by the last column in Table XXIV, the reaction is about 4 times faster with epichlorohydrin than with glycid. The ratio k_{Gl}/k_{Ep} is almost the same for Reactions III and I.

Reaction IV has been extensively studied only for glycid and hydrobromic acid. The preliminary results recorded in Table XIX, however, enable us to obtain an approximate comparison for a number of reactions. From the data in this table at 25 and 18°, the data for 20" have been calculated by the equation $d \log k/dT = 0.045$, which is shown to hold for ethylene oxide.

TABLE XXV

k_4 FOR HALOGENIC ACIDS AT ACID CONCN. 0.01 AND $t = 20°$

Ethylene oxide	HBr	5.2
Ethylene oxide	HCl	1.3
Glycid	HBr	3.3
Epichlorohydrin	HBr	1.3
Epichlorohydrin	HCl	0.27

As in Reaction III, glycid here also reacts somewhat more slowly than ethylene oxide, and epichlorohydrin again more slowly than glycid. For the ratio k_{Gl}/k_{Ep} we find

$$\left(\frac{k_{Gl}}{k_{Ep}}\right)_4 = 2.5$$

It is possible, therefore, to divide the four reactions here dealt with into two groups, one comprising Reactions I and III, in which epichlorohydrin reacts much faster than glycid, and another, comprising Reactions II and IV, in which the converse is true. Furthermore, comparing the constants of the four reactions for each oxide, the following simple relation is found to be approximately true

$$\frac{k_1}{k_2} = \frac{k_3}{k_4}$$

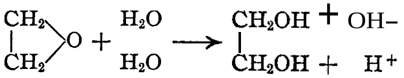
This is shown by the figures in Table XXVI, where the logarithms of the available ratios are tabulated,

TABLE XXVI

LOGARITHMS OF RATIOS

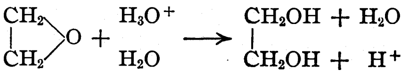
Oxide	Log k_1/k_2	Log k_3/k_4 (Cl)	Log k_3/k_4 (Br)
Glycid	$\bar{4}.1$	....	$\bar{4}.5$
Epichlorohydrin	$\bar{3}.4$	3.4	$\bar{3}.6$

An explanation of this simple relationship is afforded by the assumption of the following mechanism underlying the reactions. If in Reaction I the water molecule taken up by the oxide originates from two molecules of water, the one providing a proton and the other an hydroxyl ion



(I)

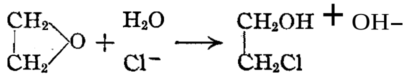
Reaction II may be described in an analogous way by simply exchanging the first water molecule which provides the proton by a hydrogen ion:



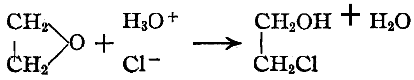
(II)

Since the H_3O^+ ion is much more acid than H_2O, the proton is more easily provided by the former, while the addition of OH^- is not affected by the presence of OH_3^+. Reaction II therefore proceeds much more rapidly than Reaction I.

If now in (I) and (II) the second water molecule is exchanged for an anion, for instance, Cl^-, Reactions III and IV appear



(III)



(IV)

and as in these reactions IV is obtained from III by again exchanging H_2O by H_3O^+, Reaction III is seen to be related to IV in just the same way as I to II. The simple relationship demonstrated by the figures in Table XXVI seems, therefore, to be well justified by the mechanism suggested.

The kinetic similarity found within the two groups of reactions here dealt with also justifies the point of view previously emphasized that catalytic reactions (Reaction II) and ordinary uncatalyzed reactions are intrinsically not different in nature.

Further insight into the reactions of the ethylene oxides may be obtainable by examining their kinetic properties in more alkaline solutions and from the stand-point of the extended theory of acid and basic catalysis. This problem is the subject of further studies in this Laboratory.

The authors are indebted to Rask-Örsted-Fondet, Copenhagen, for a grant which has made this investigation possible.

Summary

1. The ethylene oxides react in aqueous solutions in four different ways. They unite spontaneously with water to form glycols (Reaction I). The same reactions proceed, catalyzed by hydrogen ions H_3O^+ (Reaction II). They react with anions and water taking up acid (Reac-

tion III); and finally add acids directly (Reaction IV). It has been possible to separate and study separately all these reactions, using as material ethylene oxide, glycid and epichlorohydrin.

2. The hydration of ethylene oxides (Reactions I and II) is accompanied by a considerable contraction and can be followed dilatometrically. Reactions III and IV can be followed titrimetrically. A special titrimetric procedure in artificially controlled buffers was devised for following the addition of anions of strong acids (Reaction III). Reaction IV was followed by conductivity measurements.

3. The ethylene oxides exhibit apparently basic properties in certain solutions. They are, however, not bases or pseudo-bases. Their "basicity" is due to their taking up acids, which may occur through Reactions III or IV. Under ordinary conditions Reaction IV is predominant in causing basicity. The oxides may, however, also add bases and this causes acidity.

4. The hydrogen-ion catalysis (Reaction II) is determined by the concentration of the hydrogen ion. There is a considerable positive primary salt effect, which in accordance with the general theory of velocity is linear in character. Reaction III proceeds proportionally to the anion concentration and shows a slight negative primary salt effect. The velocity constant increases in the order Cl^-, Br^-, CSN^-, I^-, and in the order formate, benzoate, acetate, trimethylacetate ion.

5. The direct addition of strong acid was specially studied with glycid and hydrobromic acid. The reaction—in which two ions of opposite sign take part—was shown to follow the theoretical equation for such reactions, exhibiting an exponential negative salt effect of the predicted magnitude.

6. The constants k_1, k_2, k_3 and k_4 for Reactions I–IV satisfy approximately the equation $k_1/k_2 = k_3/k_4$. A plausible reaction mechanism has been suggested, which explains this relation.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITIES OF MOLTEN ALLOYS OF THALLIUM WITH TIN AND WITH LEAD

BY J. H. HILDEBRAND AND J. N. SHARMA

RECEIVED OCTOBER 22, 1928 PUBLISHED FEBRUARY 5, 1929

The investigation described in this paper represents a continuation of the program begun five years ago by N. W. Taylor[1] under the direction of the senior author for the determination of activities in molten alloys by a study of the e.m.f. of concentration cells. Such measurements give accurate data concerning activities over a large temperature range and are of great interest in connection with theories of solution already presented.[2] Taylor studied the alloys of cadmium with zinc, tin, bismuth and lead, and the alloy of zinc with tin. In the present investigation we have studied alloys of thallium with tin and with lead. The electrolyte used was the eutectic mixture of the fused salts of 60% lithium chloride and 40% potassium chloride, with a small amount of thallous chloride. The alloy constituted one electrode and pure thallium the other. The reaction in the cell may be represented as the transference of thallium from its pure state, where it has a unit activity, to the alloy, where its activity is a_1. The electromotive force is related to the activity by the equation $\mathbf{E}_1 = RT/\mathbf{N}_1\mathbf{F} \ln 1/a_1$, where R, T, **N** and F have the usual significance. All symbols with subscript "1" will be used in the course of this article to represent the more electropositive component of the alloy, thallium.

Materials.—The lithium chloride, potassium chloride and thallous chloride used in this research were found to be free from heavy metals. The lead was from the material purified by Hogness;[3] the tin was of known purity, and was used without further purification. About 500 g. of thallium that was at hand contained perhaps 7% of lead and small amounts of other impurities. The method used for its purification was the one used by Richards and Smyth.[4] This purified electrolytic thallium was placed in an alundum tube, which in turn was placed in a pyrex glass apparatus provided with a small inlet tube for the passage of hydrogen gas. This apparatus was heated by an electric unit and a current of hydrogen passed through. When the metal was melted, the bottom of the alundum tube was broken with the aid of a long glass rod. The pure, clean metal ran into the glass tubing provided for that purpose. Sticks of lead and tin were cast in the same manner.

Apparatus+—The cell was similar to that used by Taylor, with two cups to contain pure thallium and four other cups for alloys of varying composition. The only modification from Taylor's cell was that tungsten electrodes were soldered to heavy gold wires to lead out of the furnace and connect with the potentiometer, instead of to the

---

[1] N. W. Taylor, THIS JOURNAL, 45, 2865 (1923).

[2] Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, Inc., New York, 1924, especially Chap. XVI.

[3] Hogness, THIS JOURNAL, 43, 1621 (1921).

[4] T. W. Richards and C. P. Smyth, *ibid.*, 44, 524 (1922).

oxidizable copper wires previously used. These wires were insulated by short pieces of narrow pyrex glass tubing.

The furnace was the one used by Taylor. Temperatures were determined by two chromel-alumel thermocouples, which were calibrated against the melting points of tin, zinc and antimony. Each calibration was accurate to 1°, corresponding to 0.05 millivolt in e.m.f., which was within the limit of error.

Experimental Procedure.—The metals, whose surfaces were scraped clean and bright, were cut into small pieces. The pure thallium was put into two cups while weighed amounts of both the metals were placed in each of the remaining four cups to give alloys of known composition. The total weight of the alloy varied from about 7 to 8 g. All inlet tubes except two were sealed off and the cell was placed in the furnace. The current was turned on and a stream of hydrogen passed through the cell. In the meantime the electrolyte was prepared by weighing 60% lithium chloride and 40% potassium chloride, together with small amounts of thallous chloride and potassium hydroxide, the latter to insure the absence of hydrogen ion. When the metals in the cell had melted, the stream of hydrogen-was shut off, the clear electrolyte was immediately poured into the cell and the two remaining inlet tubes were stoppered.

The gold leads from the several compartments were connected through mercury cups to the potentiometer. This was a Leeds and Northrup (new) K type instrument, and was used with a working battery of 2 Edison cells. The electromotive force at the beginning changed more or less rapidly, but after about six or seven hours the phases became uniform in composition and the e.m.f. became constant to 0.1 m.v. The temperature of the furnace was controlled by means of the resistance and electromotive force readings were taken at intervals of one-half hour until ten or more readings were obtained. The duration of each run was usually two or three days.

In the beginning of the experimental work measurements were made on zinc–tin systems to develop the technique. The results obtained agreed with those of Taylor within the limits of experimental error.

The System Thallium–Tin.--Four runs were made on this system. The constancy of electromotive force values is illustrated in Table I, giving observed values from Run 4. Table II summarizes the observations for each run. Each e.m.f. recorded is an average of ten or more readings taken at half-hour intervals. In each recorded run, the two compartments containing the pure thallium gave zero e.m.f. against each other.

TABLE I

SUMMARY OF TYPICAL RUN (NO. 4)

Electromotive forces of thallium concentration cells in thallium–tin alloys at 414°

Thermocouple in m.v.	Temp., °C.	Cell 5–1	Cell 5–2	Cell 5–3	Cell 5–4
17.04	414	0.0857	0.1195	0.0326	0.0232
17.04	414	.0858	.1192	.0325	.0232
17.04	414	.0857	.1192	.0325	.0232
17.04	414	.0857	.1191	.0325	.0232
17.03	414	.0857	.1192	.0326	.0232
17.03	414	.0857	.1192	.0326	.0232
17.03	414	.0858	.1191	.0325	.0232
17.03	414	.0858	.1192	.0325	.0231
17.03	414	.0857	.1192	.0325	.0231
17.03	414	.0857	.1192	.0325	.0232
Average		.08573	.11921	.03253	.02318

TABLE II

SUMMARY OF OBSERVATIONS ON THALLIUM–TIN ALLOYS

Run No. 3

	N_1	0.1242	0.2107	0.3407	0.7128
414°	E	.0867	.0629	.0422	.0157
	Log γ_1	.2684	.2151	.1578	.0321
478°	E	.0979	.0712	.0507	.0194
	Log γ_1	.2544	.1917	.1272	.0170

Run No. 4

	N_1	0.05138	0.1241	0.4387	0.5645
352°	E	....	.0709	.0270	.0164
	Log γ_1	....	.3465	.1398	.0936
414°	E	.1192	.0857	.0325	.0232
	Log γ_1	.3514	.2775	.1194	.0744

Run No. 5

	N_1	0.5781	0.3944	0.15023	0.07937
353°	E	.0172	.0301	.0627	.0893
	Log γ_1	.0963	.1612	.3175	.3799
414°	E	.0225	.0374	.0756	.1047
	Log γ_1	.0731	.1300	.2701	.3325
478°	E	....	....	.0884	.1217
	Log γ_1	....	....	.2302	.2837

Run No. 6

	N_1	0.1030	0.2685	0.3722	0.6714
352°	E	.0776	.0418	.0314	.0155
	Log γ_1	.3612	.2340	.1761	.0479
414°	E	.0940	.0506	.0381	.0183
	Log γ_1	.2985	.1998	.1507	.0388
478°	E	.1097	.0604	.0462	.0210
	Log γ_1	.2518	.1660	.1195	.0320

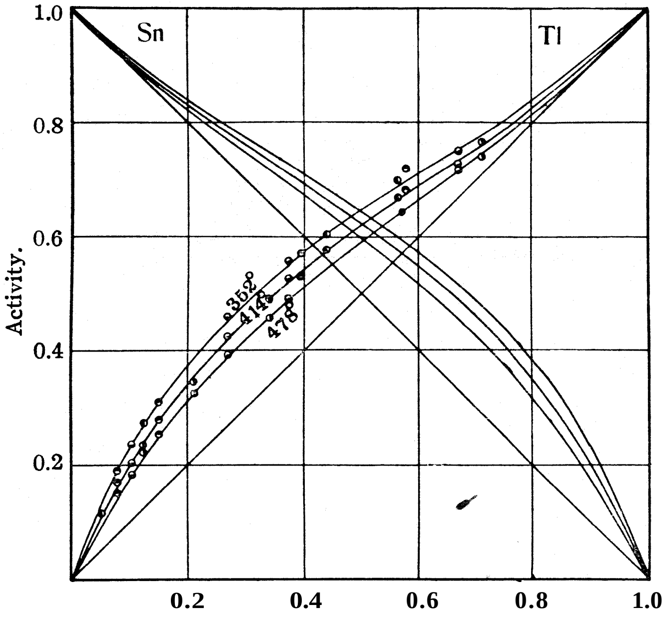
The table also gives values of log γ_1, where γ_1 is the activity coefficient, defined as a_1/N_1, where N_1 is the mole fraction of thallium, that is, the activity is taken as unity in the pure metal and not, as is customary in dealing with aqueous solutions, as the infinitely dilute solution.

The calculated values of a_1 are plotted against N_1 in Fig. 1 to show deviations from Raoult's Law. Log γ_1 is plotted against N_1 in Fig. 2. This latter plot has an important physical significance for, as the senior author has stated,[5] we may regard γ_1 as the ratio of the escaping tendency of a single molecule of thallium in solution to its escaping tendency from the pure liquid thallium. The logarithm of this ratio is zero when Raoult's law is obeyed by the solution, that is, when the intermolecular forces do not change with the composition. Due to the presence of the tin, these forces have become weaker, and hence there are positive deviations from Raoult's law.

---

[5] Ref. 2, p. 43.

The activity of the tin has been calculated by the aid of the Duhem equation, which may be expressed as follows: $N_1 \, d \log \gamma_1 = N_2 \, d \log \gamma_2$. For symmetrical curves such as these, Porter[6] has found. and the senior author has confirmed for many systems, that the relation between activity and mole fraction is often expressed by the simple equation: $\log \gamma_1 = \beta N_2^2$. The application of the Duhem equation gives for the other component: $\log \gamma_2 = \beta N_1^2$.



Mole fraction of thallium, N_1.

◑, Run 1; ◐, Run 2; 8, Run 3; ⊖, Run 4.

Fig. 1.—Activities for the system thallium-tin.

The values of $\log \gamma_1$ for the three temperatures are plotted against N_2^2 in Fig. 3. The slopes of the straight lines that can be drawn through the points give directly the several values of β given in Table III. The variation of β with T is linear and is given closely by the equation $\beta = 1.0763 - 0.00101\,T$, as shown by the excellent agreement between observed and calculated values in Table III.

TABLE III

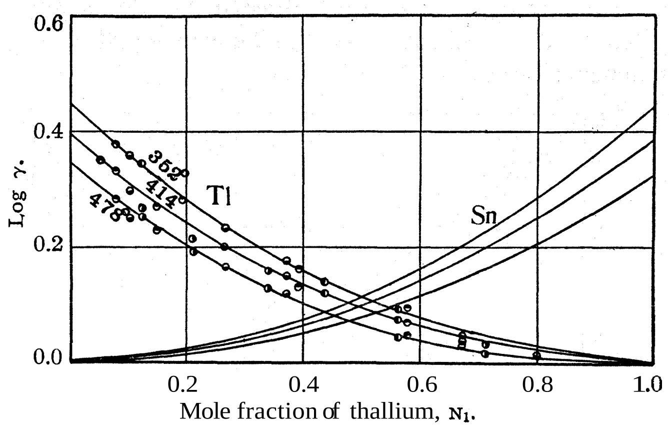
VARIATION OF β WITH T

T	Observed	Calculated	βT
625	0.4450	0.4450	278
687	.3826	.3824	263
751	.3175	.3178	239

---

[6] A. W. Porter, *Trans. Faraday Soc.*, *16*, 336 (1921).

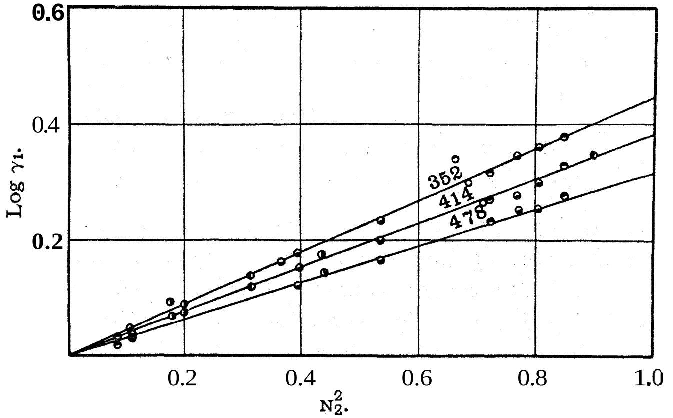
This justifies the calculation of a_1 in this system by the equation $\log a_1/N_1 = (1.0763 - 0.00101T)N_2^2$, and of a_2 by the same equation with subscripts interchanged. Table IV gives values of a_1 so calculated for certain values of N_1. The values of a_2 are given if N_2 and a_2 are read in place of N_1 and a_1.



◑, Run 1; ◐, Run 2; ◓, Run 3; ◒, **Run** 4.

Fig. 2.—Deviation of thallium–tin alloys from Raoult's law.

The table also gives the corresponding values of $\log \gamma_1$, where γ_1 is the activity coefficient, a_1/N_1, also values of the heat of transfer of thallium from pure metal to alloy, $\bar{H}_1 - H_1^{\circ}$, and the free energy of transfer of thallium from an ideal solution to the actual solution of the same concentration, $\bar{F}_1 - \bar{F}_1^i$. The latter is given by $RT \ln \gamma_1$, and the former by the expression $0.00101 \times 2.3026 \times RT^2N_2^2$, which is derived from the



◑, Run 1; ◐, Run 2; ◓, Run 3; ◒, Run 4.

Fig. 3.—Plot of logarithm of activity coefficient of thallium against square of mole fraction of tin.

expression for free energy and its temperature coefficient. We may recall, in this connection, that since there is no heat of solution in forming an ideal solution, the molal heat content of the liquid in the pure state, H_1°, is the same as its partial molal heat content in the ideal solution, $\bar{H}_1^i$; hence $\bar{H}_1 - H_1^{\circ} = \bar{H}_1 - \bar{H}_1^i$.

TABLE IV

THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THALLIUM AND TIN

t	N_1	$\log \gamma_1$	a_1	$\bar{F}_1 - \bar{F}_1^i$	$\bar{H}_1 - H_1^{\circ}$
352°	0.0	0.4443	0.0000	1305	1805
	.2	.2843	.2291	835	1155
	.4	.1599	.5781	470	650
	.6	.0711	.7067	209	289
	.8	.0178	.8335	52	72
	1.0	.0000	1.0000	0	0
414°	0.0	.3823	0.0000	1238	2182
	.2	.2447	.3514	792	1395
	.4	.1376	.5492	446	786
	.6	.0612	.6909	198	349
	.8	.0153	.8287	50	87
	1.0	.0000	1.0000	0	0
478°	0.0	.3183	0.0000	1128	2610
	.2	.2037	.3197	722	1670
	.4	.1146	.5207	406	940
	.6	.0509	.6746	181	418
	.8	.0127	.8238	45	104
	1.0	.0000	1.0000	0	0

So far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author.[7] The simplest equation applying to such a system is $RT \ln a_1/N_1 = bN_2^2$. This would apply to the system under consideration if βT were a constant, b/R. The values of βT given in Table III show that β decreases more rapidly than this. We may see the discrepancy in different but equivalent terms by recalling that a regular solution is defined in part as one which involves no entropy changes in the transfer of a component to it from an ideal solution of the same mole fraction. When this is true, the corresponding free energy and heat changes are identical, but the values in Table IV show that $\bar{F}_1 - \bar{F}_1^i$ is not equal to $\bar{H}_1 - \bar{H}_1^i$ in this case, although the two approach each other as the temperature is lowered.

An explanation of the discrepancy might be found, at least in part, if we knew the volume change involved in forming the mixture. It may prove necessary to consider the specific heat of the electrons in the alloy and in the pure metal. Although this is usually comparatively small, it may occasionally be very considerable. The previous studies of metallic solutions have ignored any influence of the free electrons, and it will be

---

[7] Hildebrand, *Proc. Nat. Acad. Sci.*, 13, 267 (1927); THIS JOURNAL, 51, 66 (1929).

interesting to determine how long this neglect can continue. We hope to make a study, in this connection, of the thermoelectric potentials of liquid alloys against pure metals.

The magnitude of the deviation from Raoult's law has been shown with other systems to correspond approximately to differences in internal pressure. We do not have the data for a close estimate of the internal pressure of thallium but the table published by the senior author shows thallium two places below tin and cadmium two above. This agrees well with the fact that the systems thallium–tin and cadmium–tin deviate to the same extent from Raoult's law, as shown by the following comparison: for the former system at 478°, when the mole fraction of tin is 0.1, its activity is 1.81; in the latter system at 483°, the activity of tin at the same mole fraction is 1.78.

TABLE V

SUMMARY OF OBSERVATIONS ON THALLIUM–LEAD ALLOYS

Run No. 1

	N_1	0.88483	0.60871	0.30793
438°	E	.0048	.0381	.0865
	Log γ	+ .019	− .055	− .108
500°	E	.0056	.0408	.0914
	Log γ	+ .017	− .051	− .085
563°	E	.0064	.0425	.0974
	Log γ	+ .014	− .041	− .077

Run No. 3

	N_1	0.07271	0.2015	0.50692	0.7037
438°	E	.1711	.1152	.0520	.0245
	Log γ	− .074	− .121	− .073	− .021
500°	E	.1813	.1221	.0557	.0262
	Log γ	− .044	− .100	− .068	− .018
562°	E	.1922	.1290	.0589	.0276
	Log γ	− .024	− .084	− .061	− .015

Run No. 4

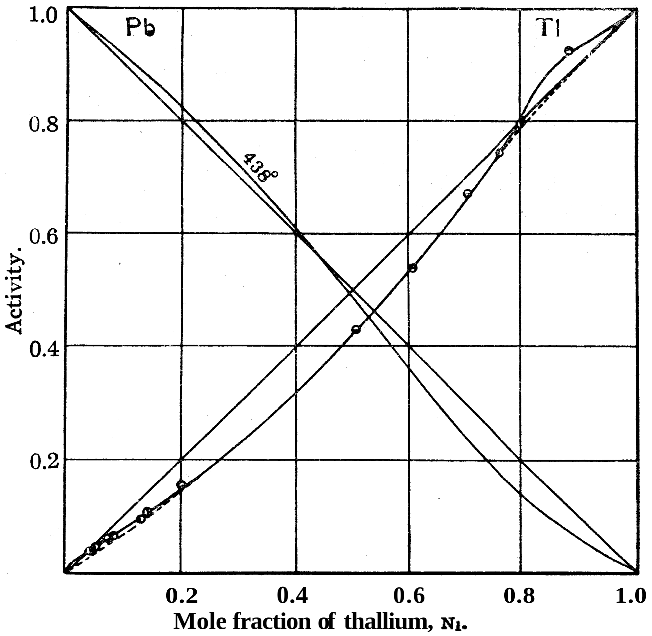
	N_1	0.04069	0.14267	0.80154
438°	E	.1936	.1356	.0142
	Log γ	+ .018	− .116	− .004
500°	E	.2193	.1457	.0142
	Log γ	− .039	− .104	+ .004

Run No. 5

	N_1	0.04541	0.0812	0.13157	0.76525
438°	E	.1840	.1660	.1413	.0180
	Log γ	− .008	− .086	− .120	− .011
500°	E	.2020	.1777	.1511	.0183
	Log γ	+ .026	− .068	− .104	− .003
563°	E	.2122	.1885	.1597	.0192
	Log γ	+ .060	− .050	− .085	− .000

The System Thallium–Lead.—Six successful runs were made on the system thallium–lead. The electromotive forces recorded in Table V are each averages of ten or more individual readings.

The activity of thallium is plotted against its mole fraction in Fig. 4, and log γ_1 is plotted against N_1 in Fig. 5. This system, although not deviating much from Raoult's law, is evidently rather complicated and strongly resembles the system lead–bismuth, investigated by Taylor,[1] showing both positive and negative deviations from Raoult's law. In order to make sure that this complication was not due to any participation of lead in the electrical process, the electrolyte was analyzed after the completion of the run. No trace of lead was found.



————, Observed; – – – –, $PbCl_2$ calcd.; 8, Run 1; 9, Run 2; ◑, Run 3; ◐, Run 4.

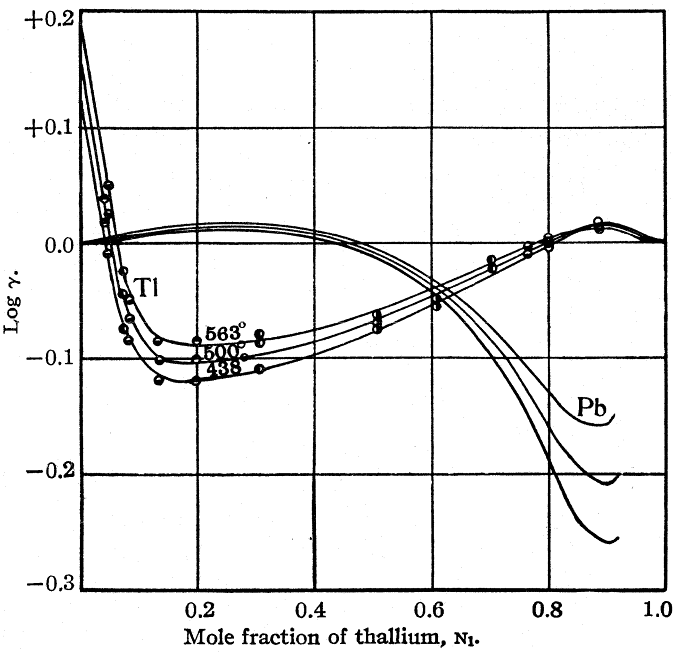
Fig. 4.—Activities for the system thallium-lead.

Taylor's investigation showed the possibility of the existence of a weak compound, Cd_3Bi_2, while the freezing-point composition diagram for the present system[8] shows the existence of the compound $PbTl_2$. It is, therefore, not surprising that both of these systems should show positive and negative deviations alike, the latter due to the formation of the compound, the former to differences in internal pressure between compound and pure components.

---

[8] Lewkonja, *Z. anorg. allgem. Chem.*, 52, 454 (1907).

Neglecting the differences in internal pressure, the effect of compound formation may be calculated by methods already developed.[9] Expressing the equilibrium constant for the reaction Pb + 2Tl = $PbTl_2$ in terms of the mole fractions of each molecular species present, we find that by assigning to it the value 2.719, we get the dotted curve shown in Fig. 4, which agrees well with the observed points except at the ends. Differ-



◑, Run 1; ◐, Run 2; ◓, Run 3; ◒, Run 4.

Fig. 5.—Deviation of thallium–lead alloys from Raoult's law.

TABLE VI

ACTIVITIES OF THALLIUM, (a_1), AND OF LEAD, (a_2)

	438°		500°		563°	
N_1	a_1	a_2	a_1	a_2	a_1	a_2
0.0	0.000	1.000	0.000	1.000	0.000	1.000
.1	.080	.919	.084	.918	.087	.912
.2	.152	.823	.157	.828	.163	.829
.3	.232	.716	.240	.720	.247	.723
.4	.320	.604	.328	.610	.336	.611
.5	.419	.488	.428	.495	.436	.495
.6	.529	.367	.538	.373	.545	.373
.7	.656	.243	.665	.248	.672	.251
.8	.790	.132	.801	.139	.810	.148
.9	.935	.055	.929	.062	.923	.069
1.0	1.000	.000	1.000	.000	1.000	.000

---

[9] Cf. ref. 2, p. 75.

ences in internal pressure, not taken into account in this calculation, of course diminish the quantitative significance of the above numerical value of K.

The activity of the lead in these alloys was calculated by the aid of the Duhem equation, using a graphic method of integration,[10] since no simple equation could be found to represent this system. The calculated values of a_2 are given in Table VI for certain values of N_1, together with the smoothed-out values for a_1.

Summary

1. The activities of thallium in liquid alloys with tin and with lead have been determined over a range of 125° by the aid of e.m.f. measurements and an equation is given for the activity in terms of mole fraction and temperature for the thallium–tin system.
2. The partial molal heat of transfer of thallium from an ideal solution to the tin solution of the same mole fraction has been calculated over a range of composition and temperature. Comparison with the free energy values calculated for the same process shows disagreement; hence, although the solution behaves as a regular solution with the respect to changes in composition, it is not regular with respect to changes in temperature.
3. The thallium–lead system, although not deviating much from ideality, shows a rather complicated behavior, almost identical with that of cadmium–bismuth alloys and which may be attributed, in part, to the presence in solution of some of the compound $PbTl_2$.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

A SIMPLE REFERENCE ELECTRODE FOR POTENTIOMETRIC TITRATIONS

BY H. H. WILLARD AND A. W. BOLDYREFF

RECEIVED OCTOBER 22, 1928 PUBLISHED FEBRUARY 5, 1929

The inconvenience connected with the use of the calomel or silver chloride half-cell as a reference electrode in potentiometric titration has long been recognized. Hostetter and Roberts[1] suggested the use of a palladium wire in place of the usual half-cell. Willard and Fenwick[2] studied a large number of bimetallic systems. Furman[3] proposed an amalgamated gold electrode as a suitable reference electrode in some oxidation–reduction reactions.

---

[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York. 1923, pp. 268 ff.

[1] Hostetter and Roberts, THIS JOURNAL, 41, 1343 (1919).

[2] Willard and Fenwick, *ibid.*, 44, 2504 (1922).

[3] Furman, ibid., 50,268,273 (1928).

Kamienski[4] used in technical electrometric determinations, especially of metals, a copper electrode in saturated copper sulfate as reference and a carborundum electrode against gold or platinum electrodes. Ball' proposed as a standard electrode a platinum wire immersed in a 3 N sulfuric acid solution (for oxidation–reduction work) or in N hydrochloric acid (for acidimetry), the electrical connection with the solution titrated being established through a wet asbestos fiber sealed securely in the end of a small glass tube. Müller[6] used in oxidation–reduction titrations an electrode system consisting of a platinum wire sealed inside of a capillary containing a very small volume of the original solution, the other electrode being a platinum wire wound around the capillary.

A very convenient and accurate method for differential potentiometric titrations has been described by MacInnes and Jones[7] and by MacInnes.[8] Modified procedures for this method are found in the papers of Roth,[9] Heckzo[10] and Hall.[11]

Among other recent methods avoiding the use of a standard half-cell in potentiometric titrations, but based on different principles than those noted above, might be mentioned those of Sandved and Backer,[12] Reissaus,[13] Foulk and Bawden[14] and Furman and Wilson.[15]

The electrode described here eliminates the use of the standard half-cell in all types of potentiometric titrations. The principle involved is extremely simple. A clean, bright platinum wire, immersed in any standard solution (oxidizing or reducing agent, acid or alkali, or a precipitating agent) will rapidly assume a perfectly definite potential.

Therefore, a very satisfactory reference electrode can be obtained by sealing a piece of smooth platinum wire into the tip of the buret (below the stopcock). It is thus in contact with the standard solution used in the titration. By dipping the tip of the buret into the solution titrated, an electrical connection is established with the indicator electrode. This "buret electrode" is shown in Fig. 1.

The tip of the buret is bent and drawn out to keep the buret out of the way and to minimize the diffusion at the point of contact of the solutions. The error due to diffusion is negligible as far as reaction inside and at the

---

[4] Kamienski, *Przemysl Chemiczny*, 11,769 (1927).

[5] Ball, *Ind. Eng. Chem.*, 19,370 (1927).

[6] Müller, *Z. physik. Chem.*, 135, 102 (1928).

[7] MacInnes and Jones, THIS JOURNAL, 48, 2831 (1926).

[8] MacInnes, *Z. physik. Chem.*, 130,217 (1927).

[9] Roth, *Z. Elektrochem.*, 33,127 (1927).

[10] Heckzo, *Z. anal. Chem.*, 73,404 (1928).

[11] Hall, Jensen and Baeckström, THIS JOURNAL, 50, 2217 (1928).

[12] Sandved and Backer, *Tids. Kemi Bergv.*, 5, 224 (1925).

[13] Reissaus, *Z. anal. Chem.*, *69*, 450 (1926).

[14] Foulk and Bawden, THIS JOURNAL, 48,2045 (1926).

[15] Furman and Wilson, *ibid.*, 50, 277 (1928).

tip of the buret is concerned because the tip is flushed out during each successive addition of the reagent, and because the concentration of the ion titrated is being constantly diminished and becomes vanishingly small near the end-point. As far as the change in potential due to diffusion is concerned, it has been shown in a control experiment that during the time between two successive additions of the titrating agent this is less than the error in measurement. The buret was filled with *0.1* N potassium bromate and the tip dipped into a solution $N/40$ with respect to arsenite. The potential between a smooth platinum wire in this solution and **the** buret electrode was measured every minute; the deviation from the initial value during five minutes did not exceed *0.2* mv.

To demonstrate the usefulness of such an electrode and the constancy of its potential, a titration was made of *0.1* *N* potassium dichromate with *0.1* N ferrous sulfate in a solution containing 25 cc. of conc. sulfuric acid in *100* cc. of solution. Three electrodes dipped into the solution: a silver chloride electrode, a bright platinum wire and a "buret electrode." The potential between any two of them could be measured. The results are shown in Table I.

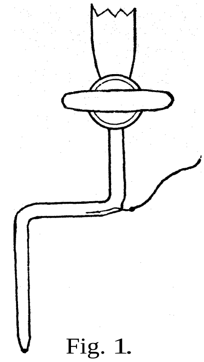


Fig. 1.

, TABLE I

POTENTIALS BETWEEN DIFFERENT ELECTRODES

Titration of approx. 0.1 N $K_2Cr_2O_7$ with 0.1 N $FeSO_4$.

$FeSO_4$ added, cc.	Potential between Pt. AgCl, mv.	Pt/buret electrode, mv.	Buret electrode/AgCl, mv.
0.0	0.8813	0.6610	0.220
4.0	.8896	.6695	.220
8.0	.8911	.6714	.220
12.0	.8930	.6724	.221
16.0	.8935	.6739	.220
20.0	.8905	.6697	.220
24.0	.8994	.6802	.219
24.5	.9000	.6801	.220
24.7	.8969	.6771	.220
24.9	.8946	.6752	.220
25.0	.8812	.6598	.221
25.1	.8418	.6243	.218
25.2	.4594	.2393	.220
25.3	.4344	.2124	.222
25.5	.4123	.1940	.218

The curves obtained by plotting potential against volume have obviously the same shape regardless of which electrode is used, but are displaced vertically from each other by an amount equal to the potential difference between the "buret electrode" and the standard half-cell. A change from the mean value of a few millivolts in the potential of the "buret electrode" is due to polarization in the process of balancing the potentiometer circuit. In some solutions (particularly 0.1 N sodium hydroxide) this polarization can become appreciable unless sufficient care is taken in balancing. A control experiment showed that this was concentration polarization.

A summary of the tests to which this method was subjected is shown in Table II. All solutions were carefully standardized and were approximately 0.1 N. The figures given represent the results of individual titrations.

In the case of permanganate, a trace of manganese dioxide forms on the platinum wire and at the tip of the buret, but the error is negligible.

TABLE II

COMPARISON OF "BURET ELECTRODE" AND AgCl ELECTRODE

Subs. titrated	Titrating soln.	$\Delta E/\Delta v$ at e.-pt. mv./cc. "Buret electrode"	AgCl electrode	Calcd., cc.	Found, cc.
$K_2Cr_2O_7$	$FeSO_4$	3850	3820	25.18	25.15
$FeSO_4$	$KMnO_4$	4270	4240	24.93	24.90
H_3AsO_3	$KBrO_3$	2900	2500	25.00	24.95
HCl	NaOH	1680	1820	18.55	18.55
HQ	$AgNO_3$	490	510	25.08	25.10

Summary

1. A simple reference electrode has been devised, consisting of a platinum wire fused into the tip of a buret.
2. The constancy of the potential of this electrode has been shown by titrations involving oxidation–reduction, neutralization and precipitation reactions.

ANN ARBOR, MICHIGAN

NOTES

A Micro Extraction Method.—For the extraction of very small amounts of material the following method may prove helpful.

A capillary of about 1–2 mm. in inner diameter and 8–10 cm. in length is filled with the liquid material (1 drop) to be extracted and an equal amount of the non-miscible extraction medium. It is then sealed at both ends and centrifuged in such a manner, that the liquid layer with the higher specific gravity is forced through the liquid layer having the lower specific gravity by having the first one at the top in the centrifugal tube and the latter on the bottom. This operation is repeated several times.

The closed capillary is then cut apart under the microscope at the zone of contact. By opening the ends both liquids, the solvent and the extraction medium, become available for examination.

By using ammoniacal aqueous solutions of alkaloids and chloroform as the extraction medium, satisfactory results were obtained by this method.

Contribution from the
Laboratory of Micro Analysis
Department of Chemistry
Washington Square College
New York University
New York, N. Y.

Joseph B. Niederl

Received August 17, 1928
Published February 5, 1929

A Brine Circulator for Cooling Condensers.—In working with low-boiling compounds it has been found advisable at times to circulate cold brine through the jackets of the condensers. Such circulation may be made continuous by the use of a simple modification of the "air lift" pump used in some sulfuric acid plants. The system gives excellent cooling and requires no attention.

The pump consists of an old condenser jacket with the lower side arm plugged up. A piece of glass tubing of about 6 mm. diameter is passed through the stopper in the top of the jacket and reaches almost to the bottom. Through the stopper in the bottom of the jacket a piece of small glass tubing of such size that it will not plug up the 6-mm. tube is passed and reaches about 2 centimeters into the 6-mm. tube. This small tube is connected to an air blast tap by a rubber tube C with a pinchcock on it to regulate the flow of air. The top side arm of the jacket is connected by rubber tubing B to the outlet of the condenser to be cooled, and the 6-mm. tube is connected by a rubber tube D to a piece of bent glass tubing hooked over the edge of a pail. This tube D should be vertical or nearly so throughout its length. The pail is filled with concentrated brine and ice and the siphon A is connected to the inlet of the condenser to be cooled. The height of the water level in the pail should be about four feet above the bottom of the pump, which may be suspended vertically over the edge of the laboratory bench.

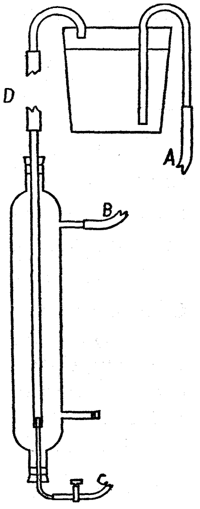


Fig. 1.—A brine circulator for condensers.

In order to start the circulation of the brine both the condenser to be cooled and the pump are filled with brine and the air is then regulated so that a steady stream of bubbles passes up the tube. The condenser jacket can be kept below zero in this manner without any difficulty whatsoever.

Contribution from the
Department of Chemistry of the
Massachusetts Institute of Technology
Cambridge, Massachusetts

Harold T. Gerry

Received September 6, 1928
Published February 5, 1929

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

MONO-ARYLGUANIDINES. I. ALPHA-PHENYLGUANIDINE[1]

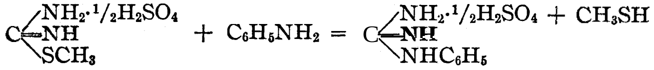
BY G. B. L. SMITH[2,3]

RECEIVED JULY 14, 1928 PUBLISHED FEBRUARY 5, 1929

Introduction

Mono-arylguanidines have received little attention or study, while diaryl- and triarylguanidines are well known and a number are produced commercially. One method only, the ammonation of cyanamide,* has been suggested for the preparation of α-phenylguanidine, the simplest compound of this series.[5]

In considering possible new methods for the preparation of α-phenylguanidine, attention was directed to the synthesis of methylguanidine[6] by the reaction between methyl-isothiourea sulfate and monomethylamine. It has been found that an excess of aniline reacts with methyl-isothiourea sulfate to form α-phenylguanidine sulfate.



$$C\begin{matrix}\diagup NH_2\cdot{}^1/_2H_2SO_4\\ =NH\\ \diagdown SCH_3\end{matrix} + C_6H_5NH_2 = C\begin{matrix}\diagup NH_2\cdot{}^1/_2H_2SO_4\\ =NH\\ \diagdown NHC_6H_5\end{matrix} + CH_3SH$$

This substance is contaminated with aniline sulfate, which cannot be removed by recrystallization from water,' but purification may be accomplished by taking advantage of the relative insolubility of α-phenylguanidine carbonate.

---

[1] A preliminary report was presented at the Philadelphia meeting of the American Chemical Society in September, 1926.

This article is respectfully dedicated by the author to Professor L. M. Dennis and will be reprinted in the Louis Monroe Dennis Quarter Century Volume to be published in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] The author takes pleasure in acknowledging the assistance of his students, M. J. Goldstein, A. E. Cleghorn and E. L. Jung.

[3] With Microscopical Studies by C. W. Mason, Assistant Professor of Chemical Microscopy at Cornell University.

[4] Franklin has pointed out the relationship existing between guanidine and a number of carbon–hydrogen–nitrogen compounds, classifying them as ammono carbonic acids, and hence the arylguanidines as ammono esters; THIS JOURNAL, 44, 486 (1922); 46, 2137 (1924); also Burdick, *ibid.*, 47, 1485 (1925).

[5] a-Phenylguanidine, its nitrate, picrate, chloroplatinate and dibenzoyl derivatives have been described: McKee, *Am.* Chem. J., 26, 22 (1901); Feuerlein, Ber., 26, 1602 (1897); Prelinger, *Monatsh.*, **13,** 97 (1892); Kampf, *Ber.*, 376, 1682 (1904).

[6] Phillips and Clarke, THIS JOURNAL, 45, 1755 (1923).

[7] The author contemplates a study of the system α-phenylguanidine–aniline–sulfuric acid–water with a view to ascertaining the exact nature of the product of this side reaction with aniline.

Experimental Part

Materials.—Methyl-isothiourea sulfate was prepared by the method of Arndt,[8] using thiourea of a high grade of purity.[9]

Crude **α-Phenylguanidine** Sulfate.—Four moles (555 g.) of methyl-isothiourea sulfate and eight moles (740 cc.) of redistilled aniline were heated to boiling under a reflux by means of an oil-bath, and the uncondensed vapors were led through a series of three wash bottles containing a 20% solution of sodium hydroxide. The system was placed under reduced pressure and the heating was continued until the solid was completely dissolved (or melted) and there was no further evolution of methyl mercaptan. On cooling the liquid solidified and was intimately incorporated with about one liter of 95% alcohol, allowed to stand with occasional shaking for twenty-four hours, filtered and the remaining solid treated in the same manner with a second liter of alcohol. This solid material when dried was generally a pale lavender in color. Further purification may be effected by decolorizing with vegetable charcoal and recrystallizing, but the sulfuric acid content of the product varies with the concentration of sulfuric acid used in recrystallizing. One speciman recrystallized from water containing 5% of sulfuric acid gave an analysis for sulfuric acid of 29.00 and for nitrogen of 18.20, indicating the presence of about 30% of aniline sulfate.

α-Phenylguanidine Carbonate.—A solution of 50 g. of crude a-phenylguanidine sulfate was neutralized with barium hydroxide and filtered. Barium hydroxide or sulfuric acid was added to the filtrate until neither was in excess and it was filtered a second time. The volume of the solution was now about 500 cc. and carbon dioxide was passed in for about two hours while the solution was cooled in an ice-bath. A granular precipitate formed which was filtered and the filtrate concentrated to half volume and treated with carbon dioxide a second and third time; yield, 30 g.

TABLE I

ANALYTICAL AND OTHER DATA OF SALTS

Compound	Analyses				M. p., °C.	Solubility	Crystal form
		Calcd., %	Found, %				
Base	N	31.11	31.38	31.25	66-68	Sol. in Bz, EtOH	Monoclinic
	C	62.22	61.66	61.79		Sl. sol. in H_2O,	
	H	6.67	6.58	6.88		CCl_4 and Et_2O	
Sulfate[a]	H_2SO_4	26.66	26.66	26.63	205	Sol. in H_2O. Sl. sol. in 95% EtOH	Monoclinic
	N	22.83	23.00	23.30			
Carbonate[a]	CO_2	13.20	12.72	12.77	138–140	Sl. sol. cold H_2O. Sol, hot	....
Hydrochloride"	HCl	21.26	21.51	21.36	...	Sl. sol. EtOAc. Sol. in all ord. solvents	Monoclinic
Nitrate	HNO_3	31.86	31.68	31.57	118–119	Sol. hot H_2O, EtOH. Sl. sol. in cold	Triclinic
Picrate	....	...	...	...	218–220	Insol. H_2O.	Orthorhombic or triclinic
Chloroplatinate	....	...	...	...	196	Sl. sol. H_2O	Triclinic

[a] Previously undescribed.

---

[8] Arndt, *Ber.*, 54B, 2236 (1921).

[9] Obtained from the American Cyanamide Company.

α-Phenylguanidine (Base).—The preparation of the base may be accomplished by treatment of a solution of one of the salts with an alkali and in general the sulfate and barium hydroxide was used. In a typical experiment 30 g. of Pure a-phenylguanidine sulfate in 100 cc. of hot water was treated with crystalline barium hydroxide and digested for one hour. After the barium sulfate was filtered off, the base separated as an oil and crystallized on seeding with a crystal of previously prepared base. The crystals were separated by filtration, washed with 5 cc. of 95% alcohol and dried in *vacuo* over phosphorus pentoxide. This material melted at 67–68° and when crystallized from benzene at 66–67°.

α-Phenylguanidine when exposed to the laboratory atmosphere takes on carbon dioxide and moisture rapidly and the melting point is raised. A sample after standing for several months was analyzed for carbon dioxide and 7.94% was found. A melting point of about 125° was invariably found when the base was dried in the atmosphere or in the oven at 50–60° and such specimens always contained carbon dioxide.

Salts of **α-Phenylguanidine.**—Salts of a-phenylguanidine may be prepared by adding the respective acid to a solution or suspension of the base or carbonate in hot water. The salt may be isolated by chilling the concentrated solution, or in the case of the hydrochloride concentrating to crystallization in a desiccator. The picrate precipitates when picric acid is added to the solutions of any salt. The extremely hygroscopic character of the hydrochloride rendered an accurate melting point determination difficult. A statement of analytical results and properties of a-phenylguanidine and its salts is given in the accompanying table.

Microscopical Notes

Base.—When prepared from the sulfate and sodium hydroxide, droplets of liquid are first formed; these coalesce and crystallize on standing. Seeding or stirring aids the crystallization. The crystals obtained are mostly rhomb-shaped tablets and dendritic forms derived from them. The acute angle of the rhombs is about 63" and is frequently truncated by a small crystal face. The tabular views of the crystals show symmetrical extinction and fairly strong double refraction, with somewhat anomalous polarization colors. They give a biaxial interference figure, the axial plane bisecting the acute angle of the rhombs; 2V is large. Edge views of the tablets exhibit oblique extinction, dispersed at about 40".

Sulfate.—The crystals are elongated tablets and flattened prisms, with symmetrical end faces making an angle of 150" with each other. Double refraction is moderately strong, with parallel extinction shown by tabular and edge views. The end views were not observed. The crystals showed biaxial interference figures, with the plane of the optic axes transverse of the long crystals; 2V large; optically positive; acute bisectrix is not perpendicular to the principal plane of the tablets.

Hydrochloride.—A number of crystallographic forms are represented: prisms, pinacoids, pyramids and domes, in differing degrees of development. The simpler crystals show a rhomb-shaped outline with beveled edges and terminal angles of either 70 or 85°. Double refraction is strong, with symmetrical extinction shown by the rhombs, and oblique extinction shown by edge views; biaxial, with the plane of the optic axis bisecting the acute angle of the rhombs, and the acute bisectrix inclined to the principal plane of the crystals; optically positive.

Nitrate.—Recrystallized from water, the crystals are in the form of oblique prisms with beveled edges, the ends truncated by a pinacoid at about 70° to their axis. The double refraction is strong, with oblique extinction exhibited by all views of the prisms. The extinction angle varies, depending on the orientation, but the maximum is about 35°; biaxial interference figure; 2V large, with plane of optic axis obliquely transverse of the crystals, optically positive,

Picrate.—Spherulites, crosses, dendrites, fine needles, prisms, and small tablets, six-sided in outline and having terminal angles of about 95° may be seen. Double refraction is very strong, with symmetrical extinction; biaxial interference figure; 2V large, with plane of the optic axis transverse of the crystals, optically negative.

Chloroplatinate.—The golden-yellow crystals are sparingly soluble in water and when precipitated show a marked tendency to form a supersaturated solution. The crystals are oblique bi-pyramids, with basal and clino-pinacoids. They show strong double refraction and all views show oblique extinction; biaxial; 2V large; probably optically positive.

Summary

The reaction between methyl-isothiourea sulfate and aniline resulted in the formation of a product consisting of a-phenylguanidine sulfate and aniline sulfate. Pure a-phenylguanidine and a number of its salts were prepared by first converting the a-phenylguanidine sulfate in the crude product to the carbonate. Certain physical and chemical properties of these substances have been described.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

MERCURATION OF RESORCINOL AND SOME ALKYLRESORCINOLS

BY REUBEN B. SANDIN

RECEIVED JULY 16, 1928 PUBLISHED FEBRUARY 5, 1929

No trimercurated derivative of resorcinol has been described in the literature and no work has been published on the mercuation of the alkylresorcinols. Dimroth has prepared a chloromercuriresorcinol and a dichloromercuriresorcinol.[1] Leys has prepared a yellow mercury resorcinol compound to which he gives the formula $HgO_2{=}C_6H_3.HgOAc$.[2] Kharasch and Chalkley[3] have examined the reactivity of acetoxymercurire-

---

[1] Dimroth, *Ber.*, 35, 2865 *(1902).*

[2] Leys, *J. pharm. chim.*, (6) 21, 1388 (1905).

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, p. 59.

sorcinol and diacetoxymercuriresorcinol dimethyl ether with ammonium sulfide. Raiziss and Prouskouriakoff[4] have prepared 4-acetoxy- and 4-chloromercuri-2-nitroresorcinol.

Regarding the relation between bactericidal power and weight of the side chain, the work of Johnson and Lane[5] and, more recently, the work of Leonard[6] have shown that the disinfectant power of the alkylresorcinols varies directly with the weight of the side chain, up to and including the hexyl group. Henry and Sharp[7] have mercurated some alkylphenols, and in their work on the bactericidal action of mercury compounds[8] it is shown that the monomercurated *p-tert.*-butylphenol apparently is less effective than the corresponding mono-mercurated *p-iso*-amylphenol.

Because it was thought that the mercurated alkylresorcinols might prove to be good bactericidal agents, and also that the study of the effect of the weight of the side chain in these compounds would prove interesting? some mercurated derivatives of ethyl- and hexylresorcinol have been prepared. Hexylresorcinol has been used because of its high phenol coefficient. Ethylresorcinol has been chosen for comparison because it is probably the easiest and cheapest alkylresorcinol to prepare. Incidentally, a trimercurated derivative of resorcinol has been prepared.

The formulas given are only tentative ones. No attempt has been made to determine the position of the mercury groups because very little information, and mostly none at all, concerning the corresponding iodine derivatives is reported in the literature.[10] It is almost certain, however, that the mercury groups are in ortho and para positions, that is, in positions 2 and 6, to the phenolic hydroxyl groups in the dimercurated alkylresorcinols, and in either one of these two positions in the monomercurated alkylresorcinols. An orientation of the mercury meta to phenolic hydroxyl is entirely improbable.[11]

Ethyl- and hexylresorcinol readily react with two molecular proportions of mercuric acetate dissolved in hot alcohol to give practically quantitative yields of the dimercurated derivatives. There is a complete removal of mercuric ion, as shown by the fact that the filtrates give no precipitate with ammonium sulfide solution. From a determination of the mercury and acetate contents and also the yields obtained, it is believed that one mercury group is an acetoxymercuri group, while the remaining mercury

---

[4] Raiziss and Prouskouriakoff, This Journal, 44, 787 (1922).

[5] Johnson and Lane, *ibid.*, 43, 348 (1921).

[6] Leonard, J. *Urol.*, 12, 585 (1924).

[7] Henry and Sharp, J. *Chem. Soc.*, 1926, 2432.

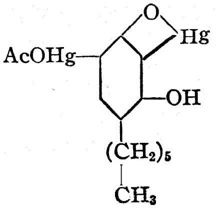
[8] Henry, Sharp and Brown, *Biochem.* J., 19, 513 (1925).

[9] The bacteriological part of this work is now proceeding.

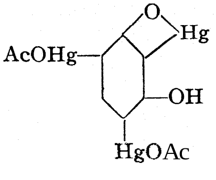
[10] It is the aim of the author to carry out the preparation of these derivatives in a later piece of work.

[11] Kharasch, This Journal, 43, 1203 (1921)

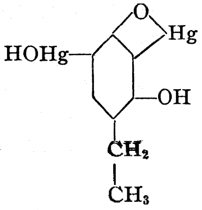
group is an anhydride group formed by the elimination of acetic acid between the phenolic hydroxyl and the acetoxymercuri group ortho to it. It is also believed that the formation of the anhydride takes place with the mercury in position 2, that is, with the mercury which is between the two phenolic hydroxyls. A suggested structure for the dimercurated hexylresorcinol would be Formula I.



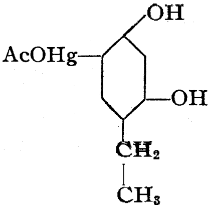
I



II



III



IV

The dimercurated alkylresorcinols prepared by the action of the alkylresorcinols on an alcoholic mercuric acetate solution are insoluble in the ordinary organic solvents, and therefore cannot be purified by crystallization. However, they usually separate in a pure state if care is taken to work with pure starting materials.

The monomercurated alkylresorcinols are prepared by adding one molecular proportion of dry mercuric acetate to two molecular proportions of the alkylresorcinol dissolved in a very small amount of hot glacial acetic acid. The compounds formed in this way are mono-acetoxymercurialkylresorcinols. They, as well as the monochloromercuri compounds, are difficult to obtain in a pure state from solvents because of their tendency to precipitate as yellow, insoluble solids. The latter are probably due to the formation of anhydro monomercurated compounds.

Resorcinol readily forms a trimercurated derivative when one molecular proportion of resorcinol is added to a hot solution of three molecular proportions of mercuric acetate in alcohol. If the proposed formula is correct, the yield is a quantitative one. In this case, too, there is a complete removal of mercuric ion from solution. The suggested formula for this compound is II.

Experimental Part

Mercuration of Alkylresorcinols*

Ethylresorcinol.—The ethylresorcinol used was prepared by the method of Johnson and Hodge.[12] One and four-tenths g. (0.01 mole) of ethylresorcinol dissolved in 10 cc. of alcohol was added to a boiling solution of 6.37 g. (0.02 mole) of mercuric acetate dissolved in 50 cc. of alcohol and 5 cc. of glacial acetic acid. Almost immediately a bright yellow solid separated and care was taken to stop heating as soon as the precipitate appeared, due to the violent "bumping" which always occurred. The reaction mixture was allowed to stand for about twelve hours. The mercurated ethylresorcinol

---

[12] Johnson and Hodge, THIS JOURNAL, 35, 1014 (1913).

was filtered off by suction and washed with hot alcohol. It was air dried and then dried *in vacuo* over sulfuric acid. The yield was **5.80** g. or 97%. The compound is insoluble in all ordinary organic solvents but is soluble in a solution of sodium hydroxide. It darkens on exposure to light and when heated at 180° it darkens but does not melt at 300°.

Anal.[13] Calcd. for $C_{10}H_{10}O_4Hg_2$: Hg, **67.40.** Found: Hg, **67.34, 67.47, 67.04. 66.85.**

On steam distillation, after decomposition by phosphoric acid, it yields **10.20%** of acetic acid ($C_{10}H_{10}O_4Hg_2$ requires **10.08%** of acetic acid), These results indicate that the compound is an anhydromercuri-acetoxymercuri-ethylresorcinol.

The above mercury compound was converted into the dichlorodimercuri-ethylresorcinol by the addition of hydrochloric acid to a suspension (it was necessary to add a few drops of alcohol to cause wetting) of the former in water. It was also necessary to stir vigorously during the addition of hydrochloric acid to prevent a localized high concentration of hydrochloric acid, which tends to break the carbon–mercury bond. The dichloro compound is a white solid and can be crystallized from alcohol. From this solvent it also tends to separate as a yellow solid which is probably an anhydromercuri derivative. The dichlorodimercuri-ethylresorcinol decomposes at 207–209° (corrected).

Anal. Calcd. for $C_8H_8O_2Cl_2Hg_2$: **Hg, 65.96.** Found: Hg, **65.82, 65.74.**

When carbon dioxide was bubbled through a sodium hydroxide solution of the anhydromercuri-acetoxymercuri-ethylresorcinol, a gelatinous precipitate was formed. This was washed repeatedly with water by decantation, then filtered off by suction and finally dried at 100° for two hours. It was obtained as a dark brown solid. The analysis indicates an anhydromercuri-hydroxymercuri-ethylresorcinol, of which the probable structure is Formula III.

And. Calcd. for $C_8H_8O_3Hg_2$: Hg, **72.52.** Found: Hg, **72.68, 72.56.**

In order to obtain a monomercurated ethylresorcinol, one mole of mercuric acetate was added, with heating and stirring, to two moles of ethylresorcinol dissolved in a very small amount of glacial acetic acid. Whiie still hot the solution was poured into water; thereupon a white solid mono-acetoxymercuri-ethylresorcinol separated. Or, if the hot solution was poured into a saturated salt solution, a white solid monochloromercuri-ethylresorcinol was formed. In both cases the compounds were crystallized from alcohol. It has been impossible so far to separate either the mono-acetoxy or the monochloro compound into two isomeric substances. Preference is given to position 6, as far as the orientation of the mercury group is concerned. Formula IV is given as the probable structure The mono-acetoxy derivative melts with charring at 163–**164**" (corrected).

Anal. of mono-acetoxymercuri-ethylresorcinol. Calcd. for $C_{10}H_{12}O_4Hg$: Hg, **50.57.** Found: Hg, **50.32, 50.30.**

The monochloro compound melts to a clear liquid at 145–146° (corrected).

Anal. of monochloromercuri-ethylresorcinol. Calcd. for $C_8H_9O_2ClHg$: Hg, **53.76.** Found: Hg, **53.50, 54.10.**

Hexylresorcinol.—The hexylresorcinol for the work was prepared according to the procedure given by Dohme, Cox and Miller.[14] The mercurated hexylresorcinol

---

[13] The analysis was carried out by decomposing the mercury compound with fuming nitric acid in a sealed tube at a temperature of 200°. The inorganic mercury in the resulting solution was then determined as mercuric sulfide.

[14] Dohme, Cox and Miller, **This Journal,** 48, **1688** (1926).

derivatives were obtained by the method already described for the mercurated ethylresorcinol compounds. In general the properties of these two series of compounds are similar. The anhydromercuri-acetoxymercuri-hexylresorcino was obtained as a bright yellow solid in a practically quantitative yield. In one case 1.94 g. (0.01 mole) of hexylresorcinol and 6.37 g. (0.02 mole) of mercuric acetate gave 6.30 g. of dimercurated derivative, or a yield of 96%. In another case 5.47 g. of hexylresorcinol and 17.95 g. of mercuric acetate gave a yield of 18.30 g., or 100%.

The compound darkens at 200° and does not melt at 300°. It darkens when exposed to light. It is insoluble in the ordinary organic solvents and is difficultly soluble in a golution of sodium hydroxide.

Anal. Calcd. for $C_{14}H_{18}O_4Hg_2$: Hg, 61.60; acetic acid, 9.21. Found: Hg, 61.27, 61.32, 61.29, 60.90; acetic acid, 9.39, 9.40.

The dichloromercuri-hexylresorcinol is a white solid and can be purified from alcohol, from which it also tends to separate as a yellow, insoluble derivative. This difficulty in purification may account for the low mercury results reported below. It melts at 137–138° (corrected).

Anal. Calcd. for $C_{12}H_{16}O_2Cl_2Hg_2$: Hg, 60.40. Found: Hg, 59.66, 59.70.

A mono-acetoxymercuri-hexylresorcinol was prepared. It was crystallized from alcohol. It forms white crystals and melts, with charring, at 177–178° (corrected).

Anal. Calcd. for $C_{14}H_{20}O_4Hg$: Hg, 44.32. Found: Hg, 44.10, 43.80.

Mercuration of Resorcinol

Trimercurated Derivative of Resorcinol.—A trimercurated derivative of resorcinol was obtained by the addition of 1.10 g. (0.01 mole) of resorcinol dissolved in 10 cc. of alcohol to a hot solution of 9.56 g. (0.03 mole) of mercuric acetate dissolved in 75 cc. of alcohol and 5 cc. of glacial acetic acid. The precipitation of the yellow trimercurated compound was almost immediate. Heating was interrupted as soon as the precipitate appeared. It was allowed to stand for twelve hours, then filtered off by suction and washed with hot alcohol. It was dried in *vacuo* over sulfuric acid. The yield was 8.21 g. or practically 100%. There is a complete removal of mercuric ion from solution. It darkens at 210° and does not melt at 300°. It is insoluble in all of the ordinary organic solvents. It is slightly soluble in a solution of sodium hydroxide.

Anal. Calcd. for $C_{10}H_8O_6Hg_3$: Hg, 72.75; acetic acid, 14.53. Found: Hg, 72.50, 72.20; acetic acid, 14.30, 14.40.

Summary

1. The preparation of some mono- and dimercurated derivatives of ethyl- and hexylresorcinol has been described.

2. The preparation of a trimercurated derivative of resorcinol has been described.

EDMONTON, ALBERTA, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF BUFFALO]

ULTRAVIOLET ABSORPTION OF PARA-AMINOBENZOIC ESTERS IN WATER SOLUTION

BY E. RAYMOND RIEGEL AND KENNETH W. BUCHWALD

RECEIVED JULY 28, 1928 PUBLISHED FEBRUARY 5, 1929

Para-aminobenzoic acid and its esters are ordinarily classed among the benzenoid compounds; their water solutions would then be expected to exhibit selective absorption in the ultraviolet with a moderate persistence referable in part to the benzene nucleus, in part to such persistence as might be ascribed to the amino group and to the carboxyl group. Without exception the eight substances which form the main part of this study possess a selective persistence of a much higher order, comparable to that of the quinonoids. The purpose of the study is to establish this fact and to explain it, at least in part. The eight substances are *p*-aminobenzoic acid, its methyl, ethyl, n-propyl and n-butyl esters, butyn, procaine and tutocaine. In the course of the discussion the data for several other substances were required and were therefore included; these are dimethyl-*p*-aminobenzoic acid, aniline and two of its salts, benzoic acid, *p*-hydroxybenzoic acid, guanidine, nitroguanidine and aminonitroguanidine. Since a number of the substances included were local anesthetics, it seemed worth while to add stovaine and alypin, in order to furnish a basis which might be of value in their identification. In the case of butyn, procaine and tutocaine, the free bases as well as the salts were measured. All solutions were water solutions, and in order to avoid the use of any other solvents, a water solution of benzene was prepared and its absorption measured. By ultraviolet we mean the region between the visible and 2100 Å.

Previous Investigations

Methyl, ethyl, n-propyl and n-butyl *p*-aminobenzoates, butyn and butyn base, procaine base, tutocaine and tutocaine base, dimethyl *p*-aminobenzoic acid, guanidine, nitroguanidine, aminonitroguanidine and alypin have not been measured previously, as far as we have been able to find, in any solvent.

Procaine, under the name novocaine, and stovaine have been studied by Brustier;[1] the measurements are reported in terms of logarithms of thickness of solution against wave lengths. A Baly tube was used.

Para-aminobenzoic acid was said by Magini to have a strong absorption band between 300 and 240 mμ which on dilution is drawn together at 260 mμ.[2]

---

[1] Brustier, *Bull. soc. chim.*, (4) 39, 1527 (1926).

[2] Quoted from Kayser, "Handbuch der Spectroscopie," S. Hirzel, Leipzig, 1905, Vol. III, p. 474.

Aniline in alcohol solutions was originally studied by Hartley[3] while aniline in alcohol with and without hydrogen chloride was studied by Baly and Collie.[4] Benzoic acid and *p*-hydroxybenzoic acid have been measured recently, with high accuracy, but in a solution of hexane with 10% ether.[5]

None of these measurements fitted exactly into our scheme, either because extinction coefficients are not given, or a comparison spectrum for each solution spectrum was not used, or the curve is incomplete, or the solvent was not water, and we have therefore made our own measurements and included them in this report.

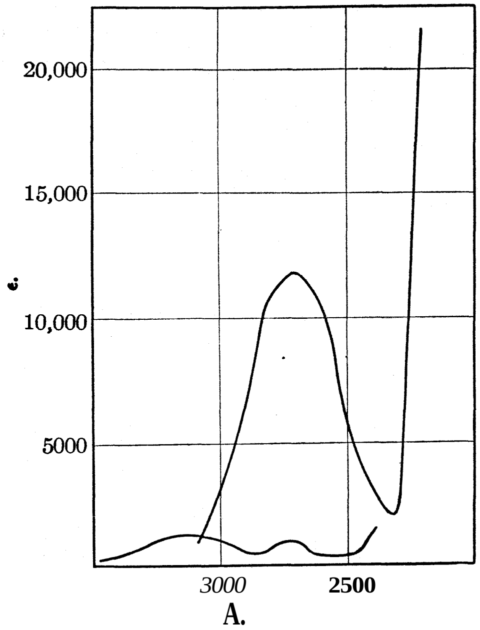


Fig. 1.—Upper curve; *p*-aminobenzoic acid; lower curve, dimethyl-p-aminobenzoic acid.

Note: Under the curve represents absorption above, transparency.

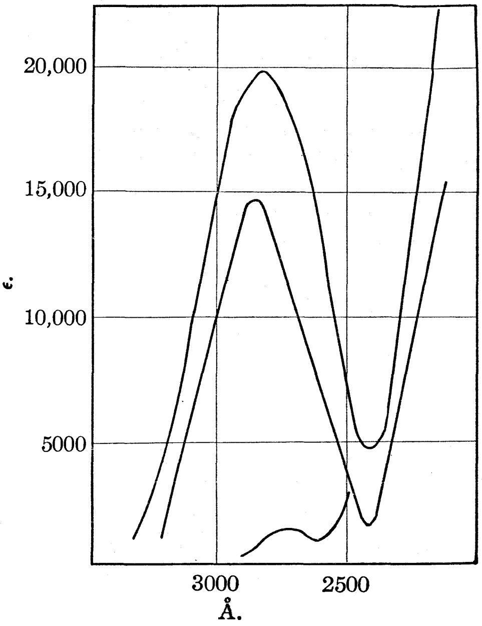


Fig. 2.—Upper curve, methyl-*p*-aminobenzoate; middle curve, ethyl-*p*-aminobenzoate (benzocaine); lower curve, alypin.

Procedure

The procedure was essentially the same as given in a previous publication, to which the reader is referred.[6]

The Schwarzschild constant in $\log t_1/t_0 = k \log I_0/I_{tr}$, the expression which links the fractions of whole revolutions of the sectors to the in-

---

[3] Hartley and Huntington, *Phil.* Trans. *Roy Soc.*, 170, i, 257 (1879), quoted from Baly and Collie's paper below.

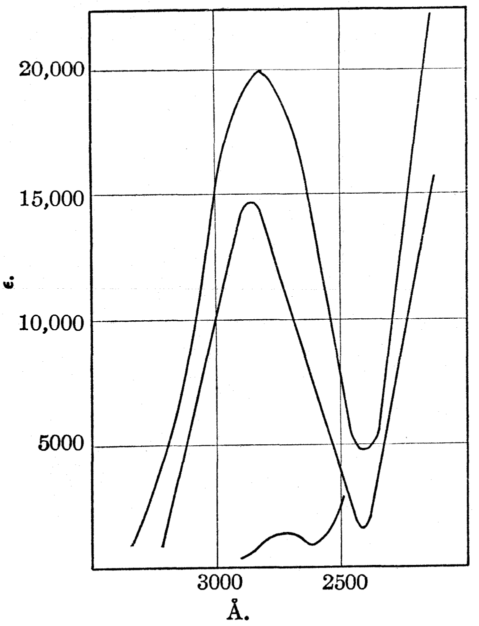
[4] Baly and Collie, J. *Chem. Soc.*, 87, *1332* (1905).

[5] Castille and Klingstedt, *Compt. rend.*, 176, 749–750 (1923).

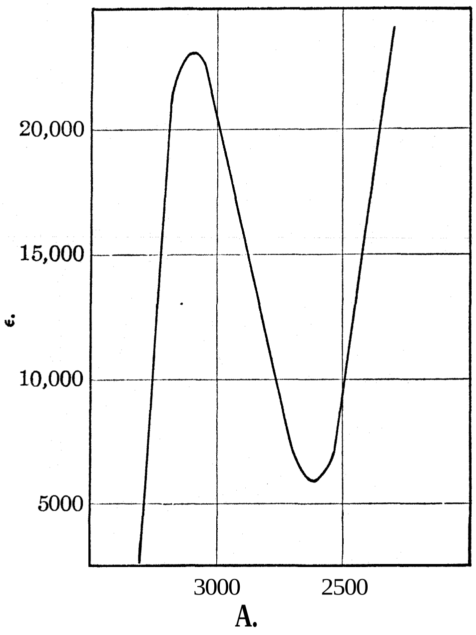
[6] Riegel and Reinhard, THIS JOURNAL, 48, 1334 (1926).

tensities, was again taken as 1; a recent paper confirms previous workers in setting this constant equal to 1, and establishes that the experimental error in the use of the Hilger sector photometer need not exceed ±2%.[7]

One departure from the previous disposition was made in that the light of the comparison spectrum was allowed to pass through a blank cell containing the same lot of solvent as the solution cell. We were led to do this because of the possible reduction in intensity which the light through the solution cell might suffer by solvent absorption, while that of the comparison spectrum would not suffer the corresponding loss. The statements regarding absorption by water are conflicting. Miller[8] states that water is "ausgezeichnet durchlassig" for the ultraviolet, confirmed by Soret, Hartley, Nichols and others. Kreusler[9] gives figures which show that freshly distilled water kept in Jena glass has very little absorption except for the region of 2000 Å. and shorter waves, but that for distilled



Pig. 3.—Upper curve, propyl *p*-aminobenzoate (propesine); middle curve, *n*-butyl/*p*-aminobenzoate (butesine); lower curve, stovaine.



Pig. 4.—Butyn.

---

[7] Baly, Morton and Riding, "The Measurement of Absorptive Power," *Proc. Roy. Soc.* London, **113A**, 709 (1927).

[8] Quoted from Kayser, "Handbuch der Spectroscopie," S. Hirzel, Leipzig, 1905, Vol. III, p. 390.

[9] Ref. 8, p. 394.

water one-half day old, kept in common glass, the absorption was near 10%. The complete series was run first without the solvent cell for the comparison spectrum, and then repeated with the cell, and observing the caution of keeping the water in pyrex flasks. While the difference in persistence values is not great, there is a difference which makes the latter procedure imperative.[10] Only the values for the measurements with the solvent cell in place are given in this paper. All solutions were at room temperature.

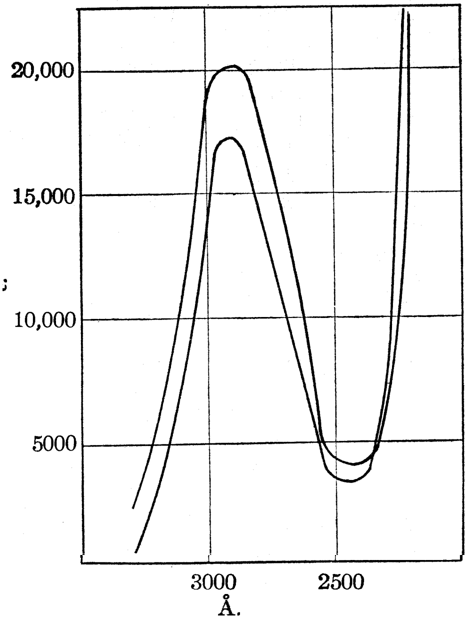


Fig. 5.—Upper curve, procaine; lower curve; tutocaine.

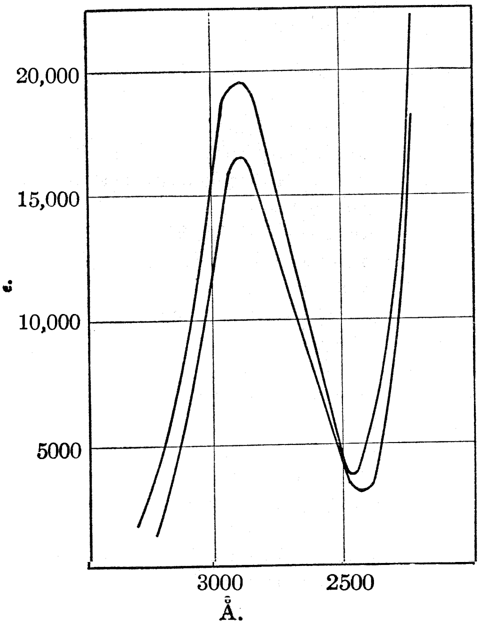


Fig. 6.—Upper curve, procaine base; lower curve, tutocaine base.

Discussion

The absorption curves of the p-aminobenzoic esters and of the free acid are clearly similar and their selective persistence is of the same order of magnitude. The values for selective persistence have been brought together in Table I; they are scaled from the original curve on millimeter paper and represent the numerical difference between the extinction coefficient for the head of the band, which is also the absolute persistence, and the extinction coefficient at the trough, where the transparency is about to cease. As will be seen from the last value in the table, the selective persistence of N-methyl-y-pyridone, a quinonoid, is surpassed by three of the p-aminobenzoic esters and approached by the other three,

---

[10] We are indebted to Dr. Shapiro of the Department of Physics, Cornell University, for this timely criticism.

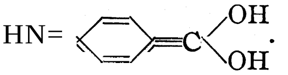
TABLE I

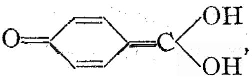
ABSOLUTE PERSISTENCES AND SELECTIVE PERSISTENCES (WATER SOLUTIONS)

Compound	Head of band. Å.	Absolute persistence	Selective persistence
p-Aminobenzoic acid	2710	11800	9700
Methyl *p*-aminobenzoate	2830	18500	13300
Ethyl paminobenzoate (benzocaine)	2850	14400	13400
Propyl *p*-aminobenzoate (propesine)	2830	19900	15100
Butyl *p*-aminobenzoate (butesine)	2850	14700	13100
Butyn	2865	19100	17100
Butyn base	2860	16700	14600
Procaine	2890	20000	15900
Procaine base	2900	19500	15700
Tutocaine	2900	17200	13700
Tutocaine base	2890	16600	13400
Dimethyl-*p*-aminobenzoic acid	2740	1000	550
Dimethyl-p-aminobenzoic acid	3130	1300	800
Aniline	2780	1430	810
Aniline hydrochloride	2815	230	110
Aniline hydrobromide	2735	320	100
Benzoic acid	2715	1030	340
p-Hydroxybenzoic acid	2500	17300	13900
Guanidine carbonate	..	...	none
Nitroguanidine	2630	14000	9700
Aminonitroguanidie	2650	16700	10700
Stovaine	2730	1300	350
Alypin	2750	1100	400
Benzene in water	2590	105	51
Benzene in water	2530	132	77
Benzene in water	2470	112	55
Benzene in water	2425	73	16
Benzene in water	2365	45	8
N-methyl-y-pyridone[a] (for comparison)	2600	16700	15500

[a] THIS JOURNAL, **48,** 1342 (1926).

as well as by the free acid. This suggests that for each of these substances most of the molecules are in the hemiquinoid form indicated by the formula



Such a view is confirmed by the low absorptive power of dimethyl-*p*-aminobenzoic acid, whose selective absorption is only 5.6% of that of the average of the first 11 items in the table, all with the *p*-aminobenzoic structure. The methyl group is generally assumed to migrate with great reluctance if at all. The absorption for aniline alone, added to that for benzoic acid alone, is insufficient to account for the selective persistence of the *p*-aminobenzoic compounds. *p*-Hydroxybenzoic acid, on the other hand, has a selective persistence about equaling the average of that of the *p*-aminobenzoic substances; like the latter, *p*-hydroxybenzoic acid may be written in hemiquinoid form, , which would explain its high persistence.

Mere para position does endow the molecule with a selective persistence of the magnitude possessed by the p-amino compounds; for example, p-xylene in alcohol has its maximum persistence at 2740 Å., namely 256, while p-cymene in alcohol has its best selective persistence at the band 2730 Å., measuring 540. The latter is the greatest persistence of *p*-substituted alkyl benzenes which we have measured.[11] It is evident that mere para position does not account for the high selective persistences reported.

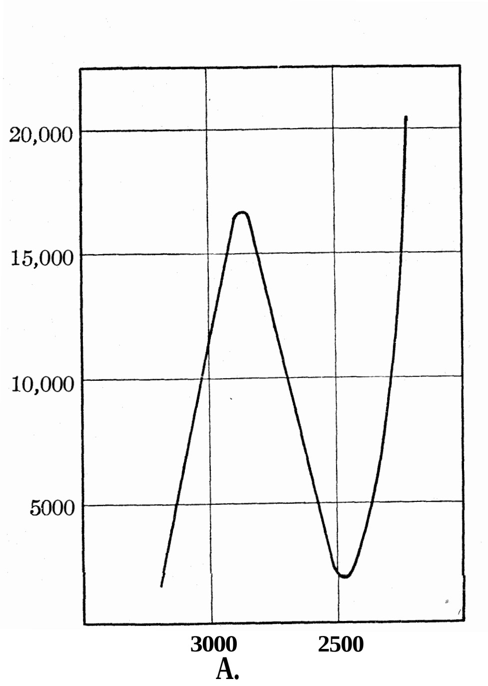


Fig. 7.—Butyn base.

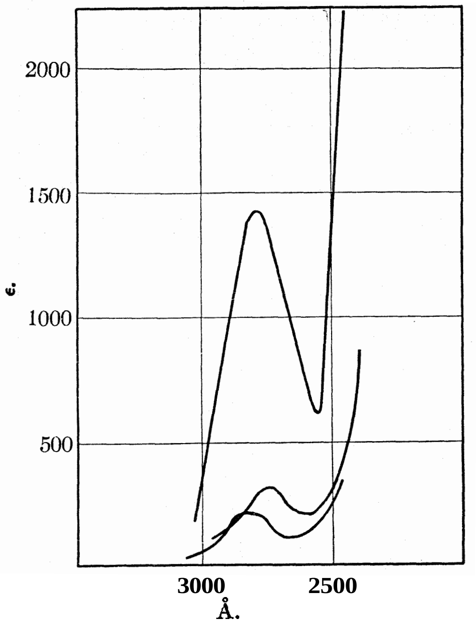


Fig. 8.—Upper curve, aniline; middle curve, aniline hydrochloride; lower curve, aniline hydrobromide.

It was expected that the free base would differ from the respective hydrochlorides or sulfates in a regular manner, but as may be seen from the table, butyn base has a selective persistence considerably lower than butyn, while procaine base has one about equal to that of procaine, and tutocaine base also has essentially the same selective persistence as tutocaine. In the case of aniline, both the hydrochloride and the hydrobromide have a selective persistence about $^1/_8$ of that possessed by the free base.

[11] These results will be embodied in a subsequent paper.

That selective absorption is not limited to ring structures is well shown by the absorption curves for nitroguanidine and aminonitroguanidine. These two substances have not only considerable selective persistence but their curves are similar in shape to that of the p-aminobenzoic compounds. Guanidine carbonate has no selective absorption, so that the selective absorption of its two derivatives must be due to the nitro group and to the disturbance in the stability of the molecule caused by its introduction. Stovaine and alypin have only inconsiderable selective persistence; their molecules contain no grouping susceptible to a hemiquinoid or quinonoid rearrangement. Benzene in water has only slight selective persistence.

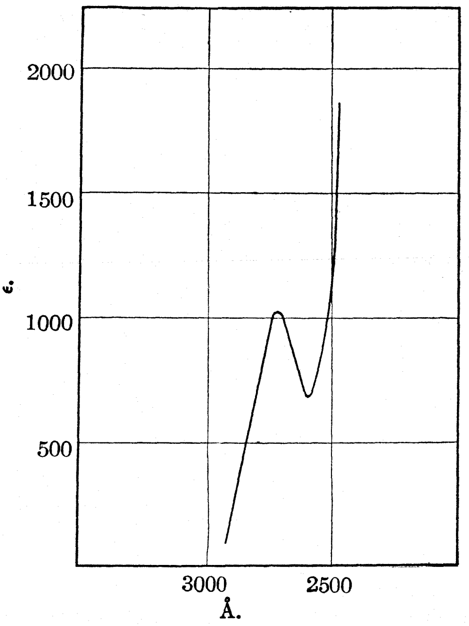


Fig. 9.—Benzoic acid.

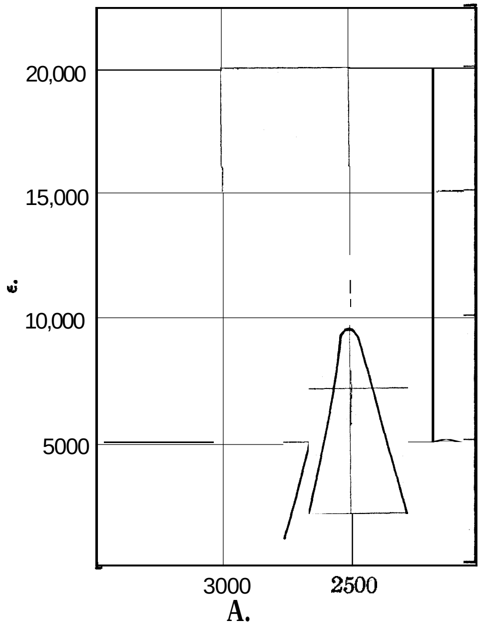


Fig. 10.—*p*-Hydroxybenzoic acid.

Cocaine in the form of hydrochloride in water solution has been measured by Castille,[12] while cocaine base in alcohol had been studied some time before that by Henri.[13] We repeated the study of the salt, using cocaine sulfate in water solution, obtaining values in agreement with those of Castille.

The base dissolved in water was also measured; the curve is not unlike that for the alcohol solution. From our results a band at 2725 Å. has absolute persistence **1400,** selective persistence **600;** while a second band at **2310 Å.** has absolute persistence **13,300** with a selective persistence undetermined because the trough of this band lies below **2100 Å.**

[12] Castille, *Bull. acad. royal med. Belg.* [5], 5, 193–200 (1925); see also ref. 1.

[13] Gompel and Henri, *Compt. rend.,* 156, 1541 (1913).

The head of the band for the *p*-aminobenzoic esters is well toward the red from the position of the head for the free acid, in agreement with the rule of Hartley. The position of the heads of the bands for the several esters with respect to each other does not show absolute agreement with the rule.

Materials

p-Aminobenzoic acid, a by-product in the manufacture of benzoic acid by the nitration of toluene, was recrystallized twice, and the absorption spectrum determined on this sample; m. p. 186° ("International Critical Tables," 187°).

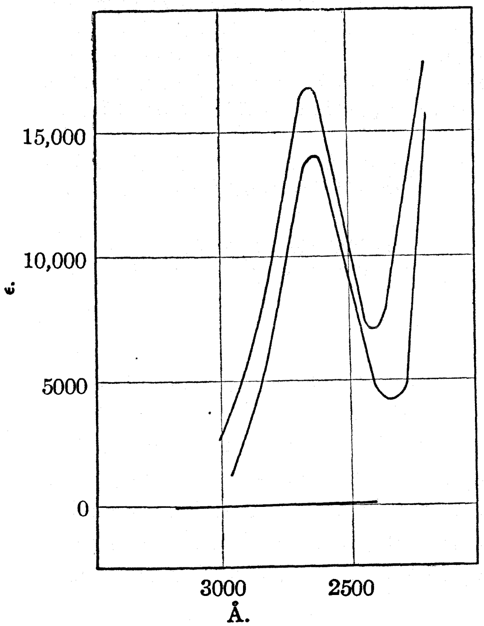


Fig. 11.—Upper curve, aminonitroguanidine; middle curve, nitroguanidine; lower curve, guanidine carbonate.

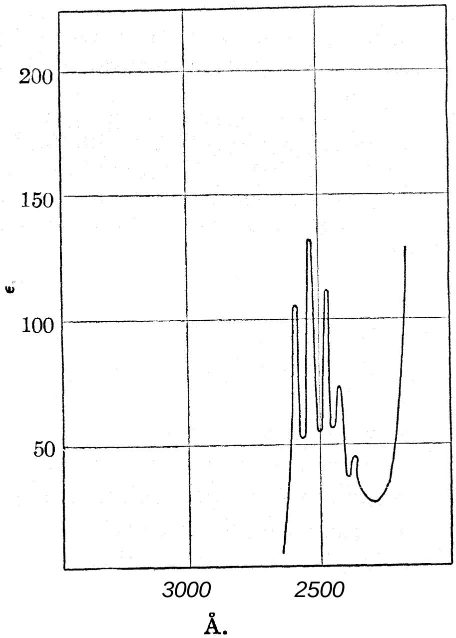


Fig. 12.—Benzene in water.

Methyl p-aminobenzoate was made from the acid by esterification with methyl alcohol in the presence of sulfuric acid; after refluxing for five hours the excess methyl alcohol was removed by distillation. The residual liquid was cooled and neutralized while ice-cold with caustic. A somewhat colored, sweet-smelling precipitate of the ester was formed; it was filtered off, washed with water and recrystallized from alcohol several times. The melting point was 112° ("International Critical Tables," 112°).

Ethyl p-aminobenzoate was the pharmaceutical benzocaine, recrystallized, with melting point 90° ("International Critical Tables," 91°).

n-Propyl p-aminobenzoate was made from the acid by esterification with *n*-propyl alcohol by the same procedure as for the methyl ester, The melting point was 75° ("International Critical Tables," 74–75°).

Butyn, procaine, tutocaine, stovaine and alypin were the pharmaceutical products; they were all recrystallized at least once and their several constants were found to agree with the literature values. The free bases for butyn, procaine and tutocaine were prepared from the salts by treating with ammonia, drying the oil first formed and, after it had hardened, crystallizing. Tutocaine base leaves the oil stage with great difficulty; we were able, however, to use a special sample prepared for this work by the Winthrop Chemical Company, consisting of well-formed crystals with melting point 98–99°. The procaine base melted at 60°, the butyn base at 33°.

Dimethyl *p*-aminobenzoic acid was made from Michler's ketone by mixing it with soda lime and heating the mixture in a retort to 350°; after the dimethylaniline had distilled off, the residue was treated with hot water and acidified with dilute acetic acid. This method is one of the two proposed by Bischoff;[14] the second one involves closed tubes. Both were tried, and the first was found to be very much superior. The crude product was recrystallized twice from 50% alcohol, giving white needles of melting point 235°, essentially the Beilstein value.

Nitroguanidine was made by dissolving guanidine nitrate in cold sulfuric acid and pouring the solution slowly into cold water;[15] long, needle-shaped crystals separate and these were recrystallized; melting point 230° ("International Critical Tables," 231°).

Aminonitroguanidine was supplied by Mr. John F. Williams of the Graduate Department, who prepared it, with Mr. Ross Phillips, for the first time.[16] The substance decomposes with explosive violence at 185°.

The remaining substances are well known and were prepared or purified by standard methods; each was tested for its physical constants, and these agreed with literature values.

Summary

1. The ultraviolet absorption of the water solutions of p-aminobenzoic acid and of seven of its esters has been determined.

2. In order to assist in the discussion, the ultraviolet absorption of several other substances was also determined. These substances are dimethyl-p-aminobenzoic acid, aniline and two of its salts, benzoic acid, p-hydroxybenzoic acid, guanidine, nitroguanidine, aminonitroguanidine, stovaine, alypin, benzene and the free bases of butyn, procaine and tutocaine, all in water solution.

3. The selective absorption of the p-aminobenzoic compounds averages 14,100, with the extremes 9700 and 15,900, while that for benzene in water solution is less than 100; hence the considerable absorption of the *p*-aminobenzoic compounds is not due to the benzenoid nucleus, but rather to a hemiquinoid state. This conclusion is confirmed by a consideration of the selective absorption of the substances listed in 2.

BUFFALO, NEW YORK

---

[14] Bischoff, *Ber.*, 22, 341 (1889).

[15] Tenney L. Davis, THIS JOURNAL, 44, 868 (1922).

[16] Phillips and Williams, *ibid.*, 50, 2465 (1928).

[CONTRIBUTION NO. 36 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE OXIDATION OF TRIBROMORESORCINOL[1]

BY TENNEY L. DAVIS AND JULIAN W. HILL

RECEIVED AUGUST 9, 1928 PUBLISHED FEBRUARY 5, 1929

A study of the oxidation of resorcinol and its derivatives is interesting because of the light which it may throw upon the mechanism of the oxidation of phenols in general, a subject already largely illuminated by the researches of Pummerer,[2] Goldschmidt,[3] Hunter[4] and others, and because of the possibility that *m*-quinones may be produced. No m-quinones are known. If products from the oxidation of resorcinol and its derivative are isolated and characterized and found to be not m-quinones, then the results will show us how the molecules have evaded the possibility of *m*-quinone formation and will, to that extent, increase our understanding of the factors which determine stable structures in aromatic and related compounds.

The oxidation of resorcinol does not appear to have been studied. Henrich, Schmidt and Rossteutscher[5] studied the oxidation by air of orcinol in alkaline solution and although they did not establish the structure of the primary oxidation product they showed that it yielded on reduction a substance which was probably pentahydroxyditolyl. Stenhouse[6] oxidized trichloro-orcinol with alkaline potassium ferricyanide and believed that he isolated a *p*-quinone, $C_7H_4Cl_2O_3$, which reduced to a hydroquinone, $C_7H_6Cl_2O_3$. He reported that he had secured corresponding results with tribromo-orcinol, trichlororesorcinol and tribromoresorcinol, but did not describe the experiments or the compounds. We find that alkali has a very destructive effect upon tribromoresorcinol,[7] and have had no success with ferricyanide as an oxidizing agent. Meyer and Desamari[8] attempted by a number of methods to prepare a m-quinone from tribromoresorcinol, but recovered the substance unchanged after shaking it in ether solution with silver oxide and anhydrous sodium sulfate, after boiling in benzene solution with lead dioxide, and after treating with nitric acid in cold glacial acetic acid solution. By the use of nitric acid in

---

[1] A summary of the Doctor's Dissertation of Julian W. Hill, Massachusetts Institute of Technology, June, 1928.

[2] Pummerer and others, *Ber.*, 47, 1472, 2957 (1914); 52, 1392, 1403, 1414, 1416 (1919); 55,3116 (1922); 58,1808 (1925); 59,2161 (1926).

[3] Goldschmidt and others, *ibid.*, 55,3194,3197 (1922); 56, 1963 (1923).

[4] Hunter and others, THIS JOURNAL, 38, 1761 (1916); 39, 2640 (1917); 43, 131, 135, 151 (1921); 48, 1608, 1615 (1926).

[5] Henrich, Schmidt and Rossteutscher, *Ber.*, 48,483 (1915).

[6] Stenhouse, *ibid.*, 13, 1305 (1880).

[7] Cf. Jackson, Am. *Chem.* J., 18,117 (1896).

[8] Meyer and Desamari, *Ber.*, 42,2814 (1909).

warm glacial acetic acid solution, they converted tribromoresorcinol into 2-bromo-4,6-dinitroresorcinol.

We have isolated three products from the oxidation of tribromoresorcinol with aqueous chromic acid and have established their relationships and probable structure.

The methods described by Benedikt[9] for the preparation of tribromoresorcinol were found to give a poor yield (65% in the best experiment) and recrystallization from dilute alcohol gave pink crystals. We have found that crystallization from chloroform yields a white product and that bromination in that medium gives pure material in practically theoretical yield. The resulting tribromoresorcinol crystallized from chloroform in white needles, m. p. 111°, and was identified by analysis.

The first oxidation experiments were carried out by adding tribromoresorcinol with stirring to a fairly strong aqueous solution of chromic acid. A brick-red crystalline powder formed at once, the mixture soon warmed up with frothing and the reaction was stopped by diluting with a large volume of water. The solid matter, recrystallized from benzene, yielded some red crystals and some unchanged tribromoresorcinol, but mostly a varnish—and the amount of product was small. Much better results were secured by oxidation in a two-phase system. An approximately 10% solution of tribromoresorcinol in benzene was shaken from time to time during three hours with a slightly smaller volume of aqueous chromic acid solution (20% CrO_3) in a bottle cooled by immersion in freshly drawn tap water. Carbon dioxide was evolved and bromine set free. Crystals separated in both phases. Removed by filtration, washed with water and dried, the product consisted of a light red-brown crystalline powder equal to 30–37% of the weight of the tribromoresorcinol which was used. Under the polarizing microscope it was found to be a mixture of a large amount of red crystals with a red-yellow pleochroism and a relatively small amount of light-colored material.

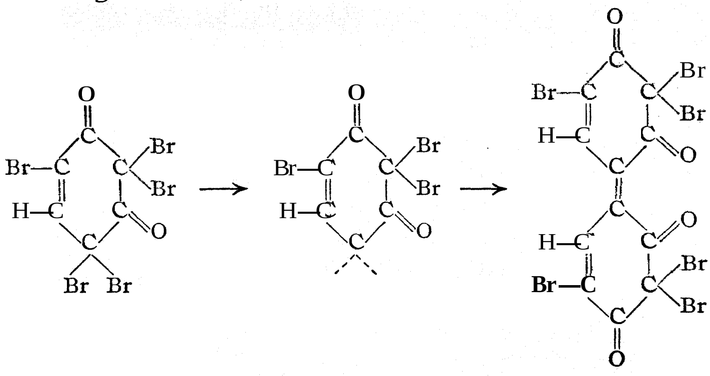
Purification of the product presented many difficulties. It was soluble in benzene, ether and glacial acetic acid, and soluble and apparently stable in cold alcohol, though with hot alcohol it yielded acetaldehyde—and the solutions in ordinary, slightly moist solvents generally yielded varnishes. Perfectly dry benzene, distilled over sodium, was found to yield crystals. By fractional crystallization from this solvent, decantation and mechanical separation of the crystals, the crude material gave splendid red crystals with a blue reflection, about 60% of its weight, and light-colored material, about 8 or 9%. The latter material by crystallization from dry benzene yielded small, white, lustrous crystals and a very small amount of yellow crystalline matter.

The yellow substance melted at 211° and was identified as tribromo-

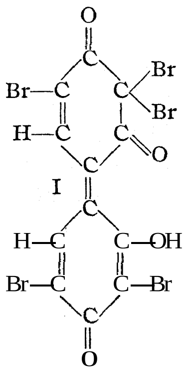
---

[9] Benedikt, *Monatsh.*, 4, 227 (1883).

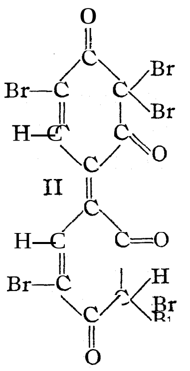
resoquinone by analysis and by comparison with known material prepared according to the method of Liebermann and Dittler[10] by heating pentabromoresorcinol at 157–160° in a current of dry carbon dioxide until bromine no longer came off, thus



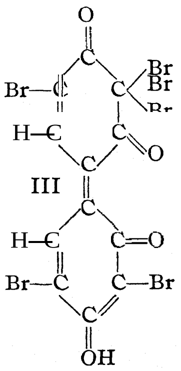
The red-colored substance which is the principal product of the oxidation of tribromoresorcinol crystallized from benzene in crystals containing benzene of crystallization, a circumstance which materially hindered its characterization. It was obtained free from solvent by replacing the benzene with ether and then refluxing with low-boiling petroleum ether, and was found by analysis and molecular weight determination to have the composition, $C_{12}H_3O_4Br_5$. Its chemical properties and transformations indicate that it has one or another of the structures indicated below.



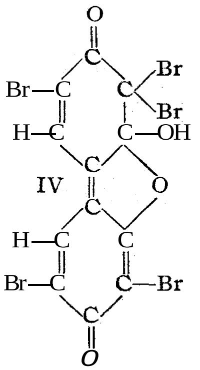
I



II



III



IV

The first three of these formulas may properly be regarded as representing one single tautomeric substance. Whether Formula IV, with the dibenzofuran[11] arrangement, really represents a substance different from this

---

[10] Liebermann and Dittler, *Ann.*, 169, 252 (1874).

[11] Behr, Arno and von Dorp, *Ber.*, 7, 398 (1874), oxidized phenol to dibenzofuran, and Pummerer, ibid., 58, 1808 (1925), obtained a dibenzofuran derivative by the low-temperature oxidation of *p*-cresol by means of alkaline potassium ferricyanide.

one may perhaps be questioned. An attempt to prove the presence of an hydroxyl group by the formation of an acetyl derivative was unsuccessful—and we consider the structure represented by Formulas I, II and III as the more probable. We have named the substance rhodo-(brom)-resoquinone (literally, the red-colored quinone-like substance from the oxidation of brominated resorcinol).

Rhodo-(brom)-resoquinone crystallizes from benzene in deep red crystals which have at first a blue reflection but lose their luster rapidly and give off a portion of their benzene, retaining some of it very tenaciously. In a melting point tube the crystals swell up, give off their benzene at 105° and melt at about 220" with decomposition and blackening. Analysis for carbon, hydrogen and bromine indicated that different batches contained different amounts of benzene. The molecular compound of rhodo-(brom)-resoquinone with ether, $C_{12}H_3O_4Br_5 \cdot C_4H_{10}O$, crystallizes from ether in pyramidal crystals of a somewhat lighter shade of red than the benzene compound. The crystals retain their luster and do not lose ether on exposure to the air. After some months they turn brown and smell of acetaldehyde. On heating they bleach and finally melt with decomposition at about 215°. The molecular compound with carbon disulfide, $C_{12}H_3O_4Br_5 \cdot {}^1/_4CS_2$, was identified by analysis. Compounds with bromoform and carbon tetrachloride were also prepared.

Rhodo-(brom)-resoquinone dissolves in dilute aqueous sodium hydroxide to form a dark green or black solution, and in concentrated sulfuric acid with a deep red color. It oxidizes the usual ketone reagents, hydrazine, semicarbazide, hydroxylamine, phenylhydrazine and dinitrophenylhydrazine, with the evolution of nitrogen. With reducing agents, sulfurous acid, sodium bisulfite, stannous chloride, metal and acid, hydrogen bromide and hydrogen iodide, it yields 3,5,3′,5′tetrabromo-2,4,2′,4′-tetrahydroxydiphenyl, identified by analysis of the substance and of its tetra-acetate for bromine and by mixed melting points of the two with known materials prepared by the reduction of tribromoresoquinone and subsequent acetylation.

In the first experiments rhodo-(brom)-resoquinone was reduced by passing sulfur dioxide into an alcohol suspension of the substance. It later appeared that the same result could be attained more rapidly and more conveniently by bubbling hydrogen bromide through a benzene solution or suspension. Bromine is liberated. Aqueous hydrobromic acid acts in the same way but much more slowly. An alcohol solution of hydrogen iodide acts rapidly, liberating iodine. A determination of the amount of iodine which was liberated supplied a means of ascertaining the oxidizing power of the substance and hence supplied further evidence of its structure.

Tribromoresoquinone was found to be reduced by the same treatment and an experiment was carried out with that substance as a check upon the accuracy of the method. The conversion of tribromoresoquinone into tetrabromotetrahydroxydiphenyl, that is, the change from $C_{12}H_2O_4Br_6$ to $C_{12}H_6O_4Br_4$, involves the addition of four hydrogen atoms and the removal of two bromine atoms, and hence requires six molecules of hydrogen iodide, thus

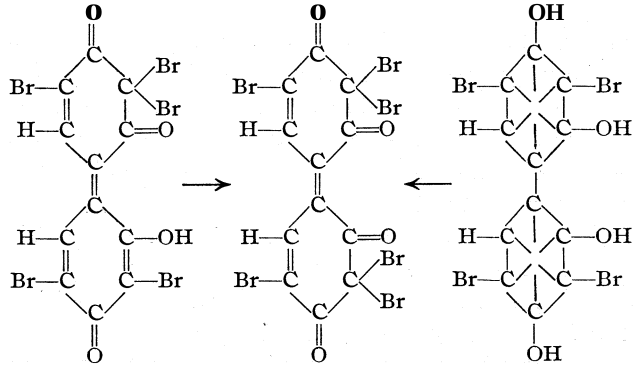
$$C_{12}H_2O_4Br_6 + 6HI \longrightarrow C_{12}H_6O_4Br_4 + 3I_2 + 2HBr$$

Similarly, if rhodo-(brom)-resoquinone has the formula which we suppose it to possess, its reduction by hydrogen iodide would take place as follows

$$C_{12}H_3O_4Br_5 + 4HI \longrightarrow C_{12}H_6O_4Br_4 + 2I_2 + HBr$$

Titrations with thiosulfate of the iodine liberated during the reduction of tribromoresoquinone and of solvent-free rhodo-(brom)-resoquinone (taken for convenience in weighing) gave results in agreement with the above equations. This establishes definitely the number of the hydrogen atoms in rhodo-(brom)-resoquinone, a number which is left in doubt by the elementary analysis. An experiment with rhodo-(brom)-resoquinone containing ether of crystallization gave a result which corresponds to the formula $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$ for the molecular compound.

Rhodo-(brom)-resoquinone yields the same reduction product as tribromoresoquinone, and the measurement of its oxidizing power suggests that it is intermediate between tribromoresoquinone and its reduction product. We find indeed that it is converted into tribromoresoquinone by the treatment by which Zincke and Schwabe[12] previously converted tetrabromotetrahydroxydiphenyl into tribromoresoquinone, namely, by the action of bromine in 50% aqueous acetic acid. The formulas show the close similarity between the compounds.



Rhodo-(brom)-resoquinone Tribromoresoquinone

Final proof that rhodo-(brom)-resoquinone is intermediate between tribromoresoquinone and its reduction product was found by producing it by the partial reduction of tribromoresoquinone. The reduction first

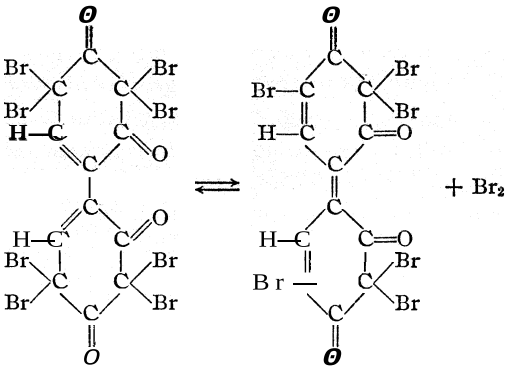
---

[12] Zincke and Schwabe, *Ber.*, 42, 797 (1909).

came about by accident. Tribromoresoquinone was allowed to stand overnight with a solution of bromine in benzene, and crusts of red crystals of rhodo-(brom)-resoquinone were found the next morning on the sides and bottom of the vessel. On longer standing the red crystals disappeared and white crystals of tetrabromotetrahydroxydiphenyl were deposited. Rhodo-(brom)-resoquinone alone was found to yield the same reduction product under like conditions. The reduction of tribromoresoquinone first to rhodo(brom)-resoquinone and finally to tetrabromotetrahydroxydiphenyl was due in this case to hydrogen bromide produced by the action of the bromine on the benzene, for solutions containing these substances did not evolve hydrogen bromide as did a solution of bromine in benzene alone. Tribromoresoquinone is not altered by long contact with a solution of bromine in carbon tetrachloride in a dry vessel closed by a glass stopper. If a cork stopper is used, the cork is attacked by the bromine to produce hydrogen bromide, and the same changes occur as in benzene solution. With hydrogen iodide tribromoresoquinone is reduced at once to tetrabromotetrahydroxydiphenyl; it is not possible, as with hydrogen bromide, to stop at the intermediate stage of reduction which is represented by rhodo-(brom)-resoquinone.

When the molecular compounds of rhodo-(brom)-resoquinone are heated they slowly lose their color and at 160–190° are entirely bleached. The white compound which is thus produced was obtained in larger quantity by heating the benzene compound at 120° for several days—small, white needles from glacial acetic acid, m. p. 228–229°. Analysis gave results which correspond to the formula, $C_{12}H_3O_4Br_5$, indicating that the substance is isomeric or polymeric with rhodo-(brom)-resoquinone. The substance is sparingly soluble in the usual solvents and its molecular weight could not be determined. It dissolves slowly in glacial acetic acid with the production of a yellow color. It liberates much less iodine from alcoholic hydrogen iodide than does rhodo-(brom)-resoquinone and resists all attempts at bromination whether in glacial or dilute acetic acid, in chloroform or carbon tetrachloride, or with undiluted bromine. We have not been able to prove its structure.

The white product from the oxidation of tribromoresorcinol was obtained by the spontaneous evaporation of its benzene solution as small, white, lustrous crystals, m. p. 227–228° with decomposition. Analysis indicated the formula, $C_{12}H_2O_4Br_8$, and its properties and reactions warrant us in assigning it the structure of tetrabromoresoquinone. Boiled with glacial acetic acid it goes into solution; the liquid quickly turns yellow and then deep orange red, bromine is given off and the liquid on cooling deposits crystals of tribromoresoquinone. The heavily brominated tetrabromoresoquinone under these conditions drops off two bromine atoms to produce the more highly conjugated, tribromoresoquinone, thus

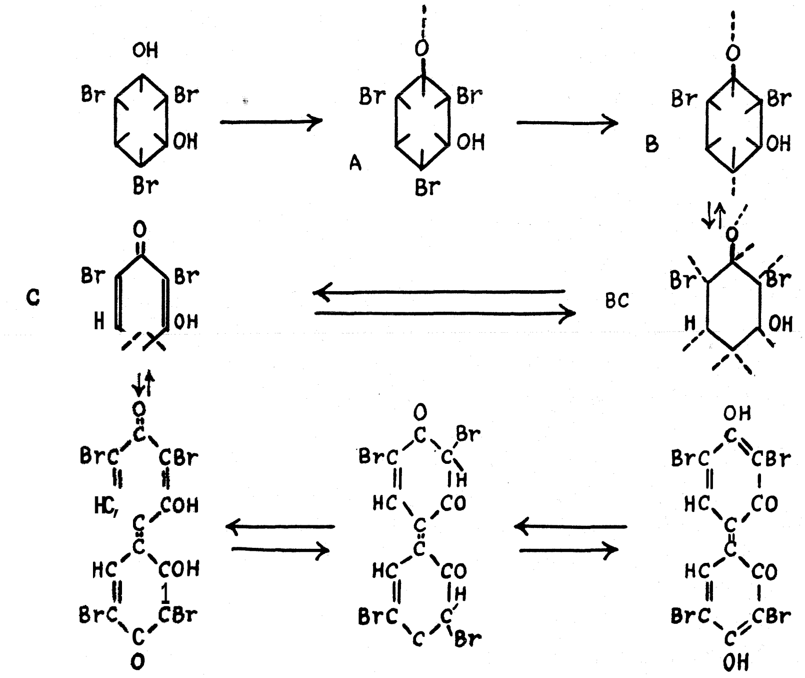


In benzene solution tetrabromoresoquinone shows but little tendency to give off bromine, yet the residues from the evaporation of such solutions to dryness are invariably tinged with yellow. When reduced in alcohol solution with aqueous stannous chloride, tetrabromoresoquinone yields 3,5,3′,5′-tetrabromo-2,4,2′,4′-tetrahydroxydiphenyl. Titration of the iodine liberated by the reaction of tetrabromoresoquinone on hydrogen iodide in alcohol solution showed that the reaction takes place as follows

$$C_{12}H_2O_4Br_8 + 8HI \longrightarrow C_{12}H_6O_4Br_4 + 4I_2 + 4HBr$$

The result served also to fix with certainty the hydrogen content of the substance, otherwise left in doubt because of the errors inherent in the determination of a small amount of hydrogen. Tetrabromoresoquinone is produced from tribromoresoquinone and from rhodo-(brom)-resoquinone when either of these substances is allowed to stand in contact with undiluted bromine. It is produced when tribromoresoquinone is shaken by machine for twenty-four hours with benzene and aqueous chromic acid containing bromine, under conditions similar to those which existed in the original oxidation experiment.

The Mechanism of the Reaction.—The work of Pummerer,[2] Goldschmidt[3] and Hunter[4] has shown it to be probable that the first step in the oxidation of phenols is the removal of hydrogen from the hydroxyl group. leading to the formation, at least momentarily, of a radical in which there is a free oxygen affinity, a radical of the sort which Hunter has designated Type A. Hunter's work has further made it probable that the formation of a radical of this type is followed, in the case of halogenated phenols, by the loss of halogen from the ring with the production of a (Type B) doubly unsaturated radical. Such Type B radicals may under oxidizing conditions yield *p*-quinones, which compounds Stenhouse, Hunter and others have indeed procured. In the absence of oxidizing agents they may combine with themselves, as Hunter found, to form polyphenylene oxides. They may also combine with themselves in another mode to form di-nuclear quinones; a possibility which is perhaps more evident if the radical represented by the Type B formula is formulated in another way (Type C below). Since Types B and C, if written with the partial valencies according to Thiele (BC below), have the same graphical representation, we think that any distinction between them is without a difference in fact and is entirely gratuitous. The action of chromic acid on tribromoresorcinol, in accordance with these hypotheses, would result in the liberation of free bromine and in the formation of a radical which would combine with itself to form the at present unknown dibromoresoquinone.



If dibromoresoquinone were a product of the oxidation of tribromoresorcinol, it would be expected to be brominated further under the conditions of our experiment. The substitution of one bromine atom would yield rhodo-(brom)-resoquinone, which would enter into molecular combination with the benzene which is present, would crystallize out and would to a large extent escape further action. If any of it should brominate, however, it would yield tribromoresoquinone and tetrabromoresoquinone, the substances which we have found. It seems probable that tribromoresoquinone was not present in the crude product of the oxidation and that the small quantity which we found was produced during the fractional crystallization by the spontaneous elimination of bromine from tetrabromoresoquinone.

Experiments

Experiments which are indicated with sufficient fullness in the foregoing are not again described in this section. Experiments are reported in the order in which their results are discussed in the first section of the paper.

Preparation of Tribromoresorcinol.—One hundred grams of resorcinol was suspended in 1500 cc. of chloroform and 432 g. of bromine was added slowly from a dropping funnel while the mixture was mechanically stirred. The clear red liquid was boiled under reflux for about an hour until it had become light yellow in color and hydrogen bromide was no longer evolved. It was treated with decolorizing carbon, distilled to one-third its volume and allowed to cool and crystallize. Concentration of the mother liquors yielded more material and the last crops were of a faint pink color. The product crystallized in handsome white needles, m. p. 111°, and was obtained in practically theoretical amount. Recrystallization from chloroform failed to raise the melting point but removed every trace of color.

Anal. Subs., 0.1964: CO_2, 0.1508; H_2O, 0.0171. Subs., 0.1230: AgBr, 0.2009. Calcd. for $C_6H_3O_2Br_3$; C, 20.69; H, 0.86; Br, 69.12. Found: C, 20.95; H, 0.97, Br, 69.51.

Isolation of the Oxidation Products.—The oxidation of tribromoresorcinol was carried out in batches, in the manner described earlier, 200 cc. of a 10% solution of the substance in benzene (previously treated with chromic acid and washed with water) and 125 cc. of aqueous chromic acid being used for each run. Gases were given off which contained carbon dioxide, as evidenced by turbidity with baryta water. After about forty-five minutes the two phases emulsified and crystalline material began to separate. Experiment showed that the yield of product did not increase after three hours, at the end of which time from 6 to 7.5 g. of crude material was obtained from each batch. The mother liquor contained free bromine, as shown by the production of tribromo-aniline, m. p. 120°, when it was distilled into aniline water.

The crude product contained a small amount of insoluble, dark-colored material which was discarded. One hundred and fifty grams, worked up as already described, yielded 90 g. of red crystals, 12 g. of light-colored material and 25 g. of residues which it was not practicable to work up. The working up of the light-colored material yielded a very small amount of the yellow constituent. The red and yellow substances were purified further by recrystallization from hot dry benzene. The white substance was obtained pure by dissolving it in a large volume of benzene and concentrating slowly. Its solubility varied very little with temperature but it separated in crystals as the volume diminished.

The Yellow Substance—Tribromoresoquinone.—*Anal.* Subs., 0.1194: AgBr, 0.1947. Calcd. for $C_{12}H_2O_4Br_6$: Br, 69.56. Found: Br, 69.40.

Rhodo-(brom)-resoquinone.—The red crystals which resulted from the fractional crystallization from benzene were shown to contain benzene by decomposing 4.5 g. of the material with aqueous potassium hydroxide and distilling into an ice-cooled receiver. The solid portion of the distillate melted at about 7°, occupied a volume of 0.90 cc. at room temperature, boiled at 79°, and on nitration yielded m-dinitrobenzene, m. p. 89.5". Two samples prepared at different times gave analytical results which correspond fairly well to one and to one-half equivalent of benzene, respectively, but the agreement is perhaps fortuitous.

Anal. Subs., 0.1976: CO_2, 0.2437; H_2O, 0.0302. Subs., 0.1916, 0.1867: AgBr, 0.2642, 0.2570. Calcd. for $C_{12}H_3O_4Br_5{\cdot}C_6H_6$: C, 31.35; H, 1.30; Br, 58.05. Found: C, 33.64; H, 1.71; Br, 58.68, 58.58.

Anal. Subs., 0.1726, 0.2001: CO_2, 0.1809, 0.2073; H_2O, 0.0196, 0.0221. Subs., 0.1315, 0.1452, 0.1597: AgBr, 0.1858, 0.2061, 0.2255. Calcd. for $C_{12}H_3O_4Br_5.{}^1/_2C_6H_6$: C, 27.69; H, 0.92; Br, 61.54. Found: C, 28.59, 28.26; H, 1.27, 1.24; Br, 60.13, 60.40, 60.09.

The molecular compound of rhodo-(brom)-resoquinone with ether was prepared by extracting a portion of the benzene compound in a Soxhlet extractor with ether which had been previously distilled over sodium. After a time crystals began to separate from the boiling liquid in the flask. When all of the material had been dissolved from the thimble, the crystals in the flask were removed. Another crop of excellent crystals was obtained by evaporating tho mother liquor almost to dryness in a vacuum over sulfuric acid. Three and five-tenths grams of the substance, decomposed by cold aqueous potassium hydroxide, yielded about 0.3 cc. of a liquid which smelled like ether and boiled at 35–37°. The alkaline liquid on distillation gave no evidence of benzene.

Anal. Subs., 0.1878, 0.2226: CO_2, 0.1916, 0.2286; H_2O, 0.0323, 0.0390. Subs., 0.1195, 0.1243, 0.1444: AgBr, 0.1651, 0,1705, 0,1985. Calcd. for $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$: C, 28.03; H, 1.90; Br, 58.40. Found: C, 27.83, 28.01; H, 1.92, 1.96; Br, 58.79, 58.37, 58.50.

The molecular compound with carbon disulfide was prepared from the benzene compound in the same way by the use of a Soxhlet extractor.

Anal. Subs., 0.01617, 0.01670: CO_2, 0.01395, 0.01451; H_2O, 0.00101, 0.00131. Subs., 0.1480: AgBr, 0.2213; $BaSO_4$, 0.0279. Calcd. for $C_{12}H_3O_4Br_5{\cdot}{}^1/_4CS_2$: C, 23.3; H, 0.48, Br, 63.5; S, 2.54. Found: C, 23.5, 23.7; H, 0.69, 0.87; Br, 63.6; *S*, 2.59.

Rhodo-(brom)-resoquinone free from combined solvent was obtained by boiling the ether compound with dry, low boiling, petroleum ether. The temperature of the heating bath did not exceed 45°. At the end of an hour and three-quarters the crystals had entirely disintegrated to a red powder. This was removed and dried in a vacuum.

Anal. Subs., 0.1631, 0.1718: CO_2, 0.1405, 0.1470; H_2O, 0.0088, 0.0102. Subs., 0.1191, 0.1418: AgBr, 0.1830, 0.2265. Calcd. for $C_{12}H_3O_4Br_5$: C, 23.56;' H, 0.49; Br, 65.47. Found: C, 23.50. 23.34; H, 0.60, 0.66; Br, 65.39, 65.22.

Mol. wt. Subs., 0.0756, 0.0736; benzene, 20.32, 20.29; *AT*, 0.032°, 0.031°. Calcd.: 611. Found: 616, 620.

Reduction of Rhodo-(brom)-resoquinone.—Ten grams of rhodo-(brom)-resoquinone with benzene of crystallization was dissolved in a mixture of 140 cc. of alcohol and 40 cc. of water, and sulfur dioxide was bubbled in until the liquid was light yellow. A precipitate separated and a further quantity of crystals appeared when the liquid was diluted with water. The yield of crude tetrabromotetrahydroxydiphenyl amounted to 5 g. of fine, violet-tinted crystals. Recrystallized from dilute alcohol with the use of decolorizing carbon, it yielded the pure product, silky white needles which melted at 277–278° after darkening at 240°.

Anal. Subs., 0.0980, 0.0960, 0.1087: AgBr, 0.1375, 0.1345, 0.1520. Calcd. for $C_{12}H_6O_4Br_4$: Br, 59.90. Found: Br, 59.71, 59.62, 59.51.

Three and one-half grams of tetrabromotetrahydroxydiphenyl was acetylated by boiling for a short time with 10 cc. of acetyl chloride and a few drops of concd. sulfuric acid and yielded 3.5 g. of the tetra-acetate, m. p. 194.5° after recrystallization from alcohol.

Anal. Subs., 0.1210, 0.1224: AgBr, 0.1294, 0.1311. Calcd. for $C_{20}H_{14}O_8Br_4$: Br, 45.58. Found: Br, 45.51, 45.57.

Iodimetric Titration of Tribromoresoquinone and Rhodo-(brom)-resoquinone.—The sample was dissolved as far as possible in 10 cc. of alcohol. Five cc. of 10% sulfuric acid and 1 cc. of 50% potassium iodide solution were then added with swirling, A white, crystalline precipitate of potassium sulfate separated. After standing for a short time, the mixture was diluted with 50 cc. of water. Most of the precipitate dissolved. The diluted solution was then titrated with standard sodium thiosulfate solution. Just before the disappearance of the yellow color, starch solution was added and the liquid was titrated to the disappearance of the blue tint. Experiment showed that if less alcohol was used, the sample blackened when potassium iodide was added. If much more alcohol was used, no blue color was produced on the addition of the starch solution.

Anal. Tribromoresoquinone. Subs., 0.1356, 0.1147: 29.75, 25.32 cc. of 0.0394 N $Na_2S_2O_3$. Calcd.: 1.179, 0.997 cc. of N $Na_2S_2O_3$. Found: 1.172, 0.998.

Anal. Rhodo-(brom)-resoquinone free from solvent. Subs., 0.0752, 0.1458: 11.25, 21.55 cc. of 0.0441 N $Na_2S_2O_3$. Calcd.: 0.493, 0.956 cc. of N $Na_2S_2O_3$. Found: 0.496, 0.950.

Anal. Rhodo-(brom)-resoquinone with ether. Subs., 0.1877, 0.1079: 24.90, 14.40 cc. of 0.0441 *N* $Na_2S_2O_3$. Calcd. for $C_{12}H_3O_4Br_5 \cdot C_4H_{10}O$: 1.096, 0.630 cc. of *N* $Na_2S_2O_3$. Found: 1.098, 0.635.

Bromination of Rhodo-(brom)-resoquinone.—One gram of rhodo-(brom)-resoquinone with benzene of crystallization was suspended in 15 cc. of 50% aqueous acetic acid and 1 cc. of bromine in 2 cc. of glacial acetic acid was added. The solid matter very soon turned yellow. After an hour it was removed, washed with water, dried in a vacuum over phosphorus pentoxide and recrystallized from benzene. The amber-colored crystals darkened at 190° and melted with decomposition at 210°. A mixture with known tribromoresoquinone of similar properties behaved in the same manner on heating.

Anal. Subs., 0.1266, 0.1429: AgBr, 0.2071, 0.2326. Calcd. for $C_{12}H_2O_4Br_6$: Br, 69.56. Found: Br, 69.62, 69.27.

Effect of Heating on Rhodo-(brom)-resoquinone.—A sample of rhodo-(brom)-resoquinone with benzene of crystallization was heated for one day at 95° and then for two days at 120°. The resulting light gray material after several crystallizations from glacial acetic acid yielded white crystals which melted at 228–229°. Although the substance appears to have the same composition as solvent-free rhodo-(brom)-resoquinone, it has only about one-half as much oxidizing power, as shown by iodimetric titration.

Anal. Subs., 0.01059, 0.01566: CO_2, 0.00902, 0.01348; H_2O, 0.00057, 0.00096. Subs., 0.0963, 0.0954: AgBr, 0.1477, 0.1466. Calcd. for $C_{12}H_3O_4Br_5$: C, 23.56; H 0.49; Br, 65.47. Found: C, 23.2, 23.5; H, 0.59, 0.68; Br, 65.27, 65.33. *Iodine Titration.* Subs., 0.01075, 0.01568, 0.02449: 3.40, 5.35, 10.30 cc. of 0.0105 *N* $Na_2S_2O_3$. Calcd.: 0.0705, 0.1028, 0.1606 cc. of *N* $Na_2S_2O_3$. Found: 0.0357, 0.0562, 0.1082.

Tetrabromoresoquinone.—*Anal.* Subs., 0.01718, 0.01303: CO_2, 0.01065, 0.00807; H_2O, 0.00100, 0.00099. Subs., 0.0940, 0.1006: AgBr, 0.1660, 0.1770. Calcd. for $C_{12}H_2O_4Br_8$: C, 16.9; H, 0.24; Br, 75.30. Found: C, 16.9, 16.9; H, 0.65, 0.84; Br, 75.15, 74.87. *Iodine Titration.* Subs., 0.0255, 0.0380: 27.21, 40.51 cc. of 0.00869 N $Na_2S_2O_3$. Calcd.: 0.240, 0.358 cc. of N $Na_2S_2O_3$. Found: 0.236, 0.352.

Conversion of Tetrabromoresoquinone to Tribromoresoquinone.—A small amount of tetrabromoresoquinone was boiled with 10 cc. of glacial acetic acid. The solution, yellow at first, became deep orange on boiling. The vapors turned starch–iodide paper blue. On cooling the liquid deposited orange needles, m. p. 203'. A sample of known tribromoresoquinone, recrystallized from glacial acetic acid, melted at 205°, and a mixture with the material from tetrabromoresoquinone melted at 204.5°. The appearance of the two under the microscope was identical.

Anal. Subs., 0.1263: AgBr, 0.2058. Calcd. for $C_{12}H_2O_4Br_6$: 69.56. Found: 69.34.

Conversion of Rhodo-(brom)-resoquinone and of Tribromoresoquinone to Tetrabromoresoquinone.—A small amount of solvent-free rhodo-(brom)-resoquinone was treated with 3 cc. of bromine, allowed to stand for two days and evaporated to dryness in a vacuum over caustic potash. The resulting material was ground up with carbon tetrachloride, washed with that solvent to free it from any traces of bromine, dried, taken up in benzene and evaporated to dryness at room temperature. The crystalline residue consisted of a mixture of white material with red crystals of rhodo-(brom)-resoquinone with benzene of crystallization. The white material was compared under the polarizing microscope with known tetrabromoresoquinone and found to be identical with it. Tetrabromoresoquinone is uniaxial negative with an w-index of about 1.776 and an e-index of about 1.700.

A similar experiment with tribromoresoquinone yielded a residue which consisted of a mixture of tetrabrnmoresoquinone with unchanged tribromoresoquinone.

A mixture of 1 g. of tribromoresoquinone, 13 cc. of 20% aqueous chromic acid, 20 cc. of benzene and 1 cc. of bromine was shaken by machine for twenty-four hours. The phases were separated and filtered and the residues were combined and recrystallized from benzene. The product consisted of small, white, lustrous crystals, m. p. 215°. A mixture with tetrabromoresoquinone, m. p. 227–228°, melted at 219–220°. A small amount of the material boiled with glacial acetic acid yielded a deep yellow solution. Examination under the polarizing microscope showed it to be tetrabromoresoquinone.

Summary

Tribromoresorcinol has been successfully oxidized by shaking a benzene solution of the substance with aqueous chromic acid.

Three products have been isolated. One of them, tribromoresoquinone, is known, having been prepared heretofore by another method. The other two, rhodo-(bromo)-resoquinone and tetrabromoresoquinone, are new. All three are dinuclear and yield the same tetrabromotetrahydroxydiphenyl on reduction.

The relationships among the three substances have been elucidated. Their oxidizing powers have been measured by titration of the iodine liberated from hydriodic acid and the results have given a precise indication of their hydrogen content.

The action of chromic acid on tribromoresorcinol appears to be first the oxidation of one hydroxyl group and the removal of one bromine atom from the nucleus. The resulting intermediate substance apparently doubles up to form the at present unknown dibromoresoquinone or 2,2′-dihydroxy-3,5,3′,5′-tetrabromodiphenoquinone. The products which have been isolated are brominated derivatives of this substance—rhodo-(brom)-resoquinone being formed by the substitution of one hydrogen atom by bromine, tribromoresoquinone by the substitution of two and tetrabromoresoquinone by the further addition of two bromine atoms.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BUFFALO AND THE JOHNS HOPKINS UNIVERSITY]

THE NITRATION OF SUBSTITUTED ANILINES[1]

BY E. RAYMOND RIEGEL, HOWARD W. POST AND E. EMMET REID[2]

RECEIVED SEPTEMBER 17, 1928 PUBLISHED FEBRUARY 5, 1929

As is well known, it is customary to acetylate an aromatic amine to protect it during nitration. In acetanilide and in its substitution products, the nitrogen is trivalent and probably remains so even in the presence of strong acids. It directs an entering group to the ortho or para position. In the case of aniline in sulfuric acid solution, the nitrogen is pentavalent and orients an entering group chiefly to the meta position. The yield of m-nitraniline is only moderate.

The object of the present investigation was to determine the effect of various substituents on the stability of aniline, *i. e.*, the resistivity toward the oxidizing action of nitric acid, during nitration in sulfuric acid solution. Certain substituted anilines give good yields of nitranilines, while others are entirely destroyed by the same nitration mixture. The substituents that have been used are the hydroxyl, carboxyl and sulfonic acid groups, with the nitro group in one case. In all, fourteen substituted anilines were studied. These are arranged in order of decreasing "persistence" of amino. The figures given represent the percentage of original amino present after nitration. We have taken no account of possible formation of nitrous acid during nitration and consequent conversion of amino to hydroxyl. The formulas given are those of probable nitration products, determined by formation of derivatives.

	Compound	%		Compound	
1	p-Aminophenol	72.6	8	m-Amino-p-hydroxybenzoic acid	0.0
2	m-Aminosalicylic acid	42.5	9	m-Amino-p-hydroxytoluene	.0
3	*m*-Amino-*p*-hydroxybenzenesulfonic acid	40.0	10	*o*-Amino-*p*-nitrophenol	.0
4	Sulfanilic acid	34.0	11	Anthranilic acid	.0
5	Metanilic acid	26.7	12	1-Amino-4-phenol-6-sulfonic acid	
6	*p*-Amino-*m*-hydroxybenzenesulfonic acid	4.8	13	m-Aminophenol	
7	o-Aminophenol	0.0	14	1-Amino-2-hydroxy-4-naphthalenesulfonic acid	49.0

Method of Nitration.—The amine was dissolved in 13 to 18 parts by weight of concentrated sulfuric acid (sp. gr., 1.84) and cooled to below 5° and the nitrating mixture of fuming nitric and concentrated sulfuric acids added, drop by drop from a buret. The

---

[1] Presented at the Detroit meeting of the American Chemical Society, September 1927.

[2] Submitted by the second author to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy, June, 1927. The work was begun at the University of Buffalo.

acid mixture was added in 10% excess based on the amount required to yield a mono-nitro derivative. It was made up to contain 0.0083 mole of nitric acid per cc. The system was stirred constantly. The mixture of acids and amine was kept for one hour at 0°, one hour at room temperature and then poured over ice. The resulting precipitate was filtered off and analyzed. Water solutions of nitration products were titrated against standard sodium nitrite in the presence of hydrochloric acid for amino contents, using starch iodide paper as indicator. Nitro groups were determined by titration against standard titanous chloride[8] and chlorine was determined whenever necessary by the Carius method.

Discussion of Results.—Nitrating aniline itself, by our method, gave a nitration product which probably consisted of a number of dinitro derivatives. After repeated extraction with alcohol and ether the product melted between 180 and 200° with decomposition. Further investigations are now being carried on to determine the identity of this material.

As regards the substitution products of aniline, the presence of hydroxyl ortho to amino seems to make the compound extremely susceptible to oxidation, while the same group in the para position gives a molecule which can be nitrated with good yield. This holds true with respect to the pairs above: 1 and 7, 2 and 8, 3 and 6. Again, the effect of the hydroxyl group in the ortho position can be overcome by the introduction of the sulfonic acid group, as witness 3 and 7, but this sulfonic acid group is a better protecting agent, in one case para to the amino (4 and 5) and in another meta (3 and 6). Evidently this is due to the presence of the hydroxyl, as Nos. 4 and 5 are sulfanilic and metanilic acids, respectively, and 3 and 6 are m-amino-p-hydroxybenzenesulfonic acid and *m*-hydroxy-*p*-aminobenzenesulfonic acid. It should be noted that p-hydroxy-aniline sulfonated spontaneously, during the reaction, and its resistance to decomposition may be due in part, at least, to the introduction of the sulfonic acid group.

The question arises as to why there should be such a difference in resistance toward the oxidizing action of nitric acid between ortho and para aminophenols and their derivatives.

Conclusions.—*o*-Aminophenol and its derivatives are unstable in the presence of a strong oxidizing agent such as fuming nitric acid, *o*-aminophenol itself going to pieces. *p*-Aminophenol is capable of giving a good yield of nitro-aminophenolsulfonic acid under the conditions holding in our work. Assuming the most stable configuration of the benzene ring to be that in which alternate carbons are similarly polarized, an electronegative group can be said to direct an entering group to the ortho or para position, while an electropositive group directs meta. This holds qualitatively. p-Aminophenol directs both sulfonic acid and nitro to the positions ortho to hydroxyl, thus giving evidence that hydroxyl is the determining factor. The amino tends in this case to adopt an electro-

---

[8] Thornton and Wood, *Ind. Eng. Chem.*, 19, 150 (1927).

positive character, at least in a relative sense. We assume that the resistivity of the ring in this case is due to the coincidence between the directive effects of the two groups, at least in part, and that the two groups when ortho to each other do not succeed in adopting such distinctly opposite polarity because of their proximity to each other.

Materials

p-Aminophenol was obtained from the Eastman Kodak Co.; NH_2, 14.34%.

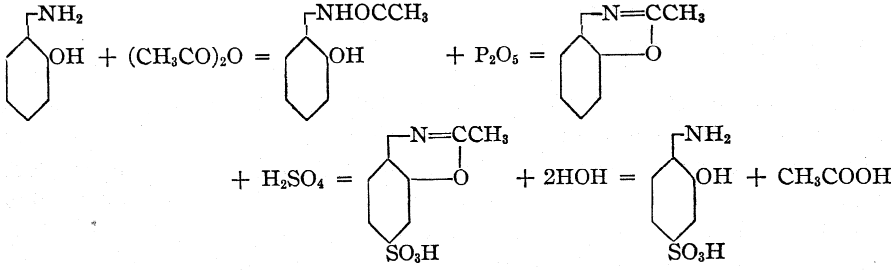
m-Aminosalicylic acid was made by coupling salicylic acid with benzene diazo chloride and reducing the azo compound with stannous chloride and hydrochloric acid.[4] The hydrochloride melted at 236°; Cl, 18.61. The free amine melted at 250–260°; acetyl derivative at 218°.[5]

m-Amino-p-hydroxybenzenesulfonic acid was obtained from the National Aniline and Chemical Co., and from the Wilbur White Chemical Co.; NH_2, 8.52%, S, 15.93; the anilide melted at 203°.[6]

Sulfanilic acid was obtained from the Eastman Kodak Company; NH_2, 9.42%.

Metanilic acid was obtained from the Eastman Kodak Company; NH_2, 9.16%.

1-Amino-6-hydroxy-4-benzenesulfonic acid was made by a method which is outlined in the literature but not in detail. o-Aminophenol, 85 g., was treated with 190 g. of acetic anhydride and the cooled product sucked dry and desiccated. This acetylaminophenol (40 g.) was then distilled off at 200° with phosphorus pentoxide. There was about 20 cc. of oily product.[7] This gave us ethenyl-o-aminophenol, of which 20 g. was placed in a ten-inch test-tube and treated with 24 g. of fuming sulfuric acid ("163%") drop by drop, the test-tube being immersed in a freezing mixture of ice and salt and the system stirred. The entire sulfonation mixture was allowed to stand for one hour and then thrown into ice water. The resulting solid was sucked dry and hydrolyzed by boiling water (400 cc.); yield, 13 g. of blue-black needles, melting after recrystallization from water at 205–210° with decomposition; NH_2, 8.66%.



o-Aminophenol was made by nitrating phenol and reducing, checking with material from the Eastman Kodak Company.

1-Amino-6-hydroxy-3-benzoic acid was made by coupling p-hydroxybenzoic acid with benzene diazo chloride and reducing with tin and hydrochloric acid, then comparing the product with one made by nitrating p-hydroxybenzoic acid and reducing with tin and hydrochloric acid; melting point, 226°; NH_2, 10.72%. In only one run

---

[4] Fischer, *Ber.*, 32, 81 (1899).

[5] Grandmougin, *ibid.*, 39, 3930 (1906).

[6] Post, *Ann.*, 205, 51 (1880).

[7] Friedländer, Vol. IX, p. 148 (German Patent 197,496); Bücherer, "Lehrbuch der Farbenchemie."

were we able to do this with the free acid; all subsequent runs were made with the methyl ester.[8]

1-Amino-3-methyl-6-hydroxybenzene was made by dissolving 21.6 g. of p-cresol in 36 g. of sodium hydroxide and 60 cc. of water. To this was added benzene diazo chloride made by titrating a solution of 18.6 g. of aniline in 150 cc. of hydrochloric acid (1:1) with 13.8 g. of sodium nitrite in 35 cc. of water. The precipitated azo compound was reduced by covering with a solution of 113 g. of stannous chloride in 119 g. of hydrochloric acid and gently warming. The product was precipitated by pouring into concentrated hydrochloric acid solution, the process being repeated to eliminate aniline hydrochloride. The free base was obtained by boiling with water; m. p. 129"; NH_2, 12.58%.

I-Amino-3-nitro-6-phenol was made by the reduction of dinitrophenol; m. p. 136°.[9]

o-**Aminobenzoic** acid was purchased from the Eastman Kodak Company; NH_2, 11.71%.

1-Amino-4-phenol-2-sulfonic acid was made by treating phenol with nitrous acid and then with sodium bisulfite; m. p. 270°.[10]

m-Aminophenol was purchased from the Eastman Kodak Company.

1-Amino-4-naphthol-2-sulfonic acid was purchased from the National Aniline and Chemical Co.

Identification of Nitration **Products.**—*p*-Aminophenol gave $C_6H_2(1)NH_2(3)SO_3H$-(4)OH(5)NO_2; derivative with dinitrochlorobenzene a red powder;[11] nitration product: NH_2, 6.82%; NO_2, 19.06%.

1-Amino-4-hydroxy-3-benzoic acid gave $C_6H_2(1)NH_2(3)COOH(4)OH(5)NO_2$; NH_2, 8.91%; NO_2, 21.81%.

1-Amino-6-phenol-3-sulfonic acid gave $C_6H_2(1)NH_2(3)SO_3H(6)OH(5)NO_2$; derivative with *β*-naphthol a brown powder;[12] nitration product: NH_2, 6.79%; NO_2, 18.37%.

p-**Aminobenzenesulfonic** acid gave $C_6H_3(1)NH_2(4)SO_3H(5)NO_2$($NH_2$, 7.34%); **de**rivative with salicylic acid a yellow-green material.

m-**Aminobenzenesulfonic** acid gave probably mostly unchanged amine and some m-phenolsulfonic acid (NH_2, 8.38%); derivative with diazotized benzidene and Gamma **Acid** a trace of black powder.[13]

1-Amino-6-phenol-4-sulfonic acid gave $C_6H_2(1)NH_2(3)NO_2(4)SO_3H(6)OH$; NH_2, 6.71%; NO_2, 18.87%.

Summary

Fourteen substituted anilines have been nitrated with mixed acids under the same conditions. Great differences in stability have been found; some groups seem to stabilize the molecule, *i. e.*, render it more resistant to the oxidizing action of the nitric acid, while others bring about its destruction. The influence of the groups depends on their position—two electronegative groups para to each other seem to make the resultant molecule more resistant to oxidation.

BALTIMORE, MARYLAND

---

[8] Friedländer, Vol. VI, p. 1153 (German Patent 111,932).

[9] Auwers and Rohrig, Ber., 30, 992 (1897); Laurent and Gerhardt, *Ann.*, 75, 68 (1850).

[10] Schultz and Stable, *J. prakt. Chem.*, (2) 69, 334 (1904); Friedländer, Vol. III, p. 57 (German Patent 71,368).

[11] Chem. *Centr.*, II, 656 (1900); German Patent 113,337.

[12] Friedlander, Vol. VII, p. 419.

[13] Friedlander, Vol. XI, p. 419.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE POLYHYDRIC ALCOHOL–POLYBASIC ACID REACTION. I. GLYCEROL–PHTHALIC ANHYDRIDE

BY R. H. KIENLE AND A. G. HOVEY

RECEIVED SEPTEMBER 22, 1928 PUBLISHED FEBRUARY 5, 1929

Introduction

The tendency of the organic chemist to discard the tarry residues or resinous products of a reaction and to explain them away by merely mentioning their formation is unfortunate. It is quite probable that in the study of resin formation many new ideas of space chemistry will be brought forth which, although not revolutionary, will simplify our concepts of materials regarded as complex and at the same time bring about a better correlation between organic chemistry, colloidal phenomena and statistical mechanics.

Although the resinous products of the polyhydric alcohol–polybasic acid reactions have been in commercial application for some time, no systematic study of the reactions has been made until the last four years.

It is probably safe to say that a resinous product results whenever *a* polyhydric alcohol and polybasic acid are heated together. This has never failed to happen when such characteristic aliphatic alcohols as glycerol, ethylene glycol and mannite have been heated with characteristic polybasic acids as phthalic anhydride, phthalic, isophthalic, tartaric, malic, succinic, citric, sebacic, diphenic[1] and naphthalic[1] acids.

The properties of the resinous products and the methods of promoting the reactions are so similar that any information obtained on the glycerol–phthalic anhydride reaction is very likely to have useful application to the others.

Historical

Although Berzelius reported the formation of a resin from tartaric acid and glycerol in the early days, it was not until 1901 that the reaction between glycerol and phthalic anhydride was reported by Watson Smith.[2] Between 1910 and 1915, M. J. Callahan[3] performed numerous experiments as a result of which new and useful resins were made which showed possibilities for commercial applications. At the same time, W. C. Arsem, E. S. Dawson, Jr., and K. B. Howell[4] studied the general reaction, substituting other alcohols and acids for glycerol and phthalic anhydride;

---

[1] Downs and Weisberg, U. S. Patent 1,667,197.

[2] Watson Smith, J. *Soc. Chem. Ind.*, 20, 1075 (1901).

[3] M. J. Callahan, unpublished data and such patents as U. S. Patents 1,108,329 and 1,108,330.

[4] W. C. Arsem, E. S. Dawson, Jr. and K. B. Howell, unpublished data and such patents as U. S. Patents 1,098,777; 1,119,592; 1,098,728; and 1,141,944.

and also the effect produced when other ingredients are added. Since 1924 the authors have been performing quantitative experiments which are probably yielding the first kinetic data on the poly-ester reaction.

Materials

Pure phthalic anhydride was obtained by melting C. P. phthalic anhydride (Selden Co.) in an electrically heated glass container over which a current of dry air was passed which conducted the vapors into a cooled bulb, where dusty cobwebs of pure phthalic anhydride were deposited. The final product had a melting point of 131.8°.

The best water-white glycerol available had a density of 1.2561 by pycnometer measurement, which corresponds to a purity of about 97.7% according to the tables of Bosart and Snoddy.[5] This glycerol was vacuum-distilled in air-tight glass apparatus. Wherever a rubber stopper was used it was isolated from the vapors by thick tin foil, so that no distillate could escape from the rubber into the vapors of the glycerol. Anhydrous sodium sulfate was placed in the distilling flask together with some glass beads to prevent bumping. Hydrogen was passed through a capillary jet which served both to prevent oxidation and minimize bumping. Only the distillate between 160 and 200° was used and redistilled. The final product had a d_{25}^{25} of 1.2598, corresponding to a purity of 99.2% according to Bosart and Snoddy.

Experimental

I. Study of the Products of the Reaction.—If the reaction involves no other mechanism than that of simple esterification, there should be no other products than esters and water. In watching the reaction, however, the most readily noticed phenomenon is the evolution of a white sublimate, shown to be phthalic anhydride, which results from the fact that the reaction takes place at a temperature where the vapor pressure of the anhydride is high. Because of the low apparent density of the sublimed phthalic anhydride, it appears that considerable quantities are evolved, but there actually is relatively very little by weight.

The apparatus which was used to study the products of formation is shown in Fig. 1. The Erlenmeyer flask, heated by a Bunsen burner, contained the reaction mixture and was connected to three traps A, B and C, which were to collect solid, liquid and gas, respectively.

Trap A consisted of a tared flask, Trap B a tared flask connected to a water-cooled condenser and Trap C, a tared flask submerged in liquid air. The circulation of the vapors from the reaction mixture was insured by introducing dry air free from carbon dioxide through a calibrated flowmeter (about 2 bubbles per second) into the reaction flask. As a precaution to prevent the collection of material in the glass tube between the reaction flask and Trap A, a small heating unit of nichrome wire was wound around it.

The reaction mixture, consisting of 46 g. of glycerol and 111 g. of phthalic anhydride, was gradually warmed up to 210° in two hours and twenty-two minutes. After cooling the reaction flask, Trap A was found to contain 7.0 g. of material, most of which was a colorless liquid, water, together with white crystals. On opening the flask a sharp odor also was noticed. The contents of the flask was titrated with $N/25$ potassium hydroxide solution, using phenolphthalein as an indicator. There was found the equivalent of 0.085 g. of phthalic anhydride.

---

[5] Bosart and Snoddy, Ind. *Eng. Chem.*, 19, 506–510 (1927).

Any increase in weight of Trap B was found to be less than the order of the accuracy of the experiment Trap C contained approximately *0.5* g. of white crystalline solid which melted at 0° to a clear white liquid, probably water although the sharp odor was noticed in this flask also. The water gave no aldehyde test (rosaniline) until near gelation. The reaction mixture itself gave no aldehyde test until gelation.

This, together with the fact that acrolein and phthalic anhydride do not form a resin, makes very doubtful the suggestion of Barry, Drummond and Morell,[6] that intermediate aldehyde formation is the mechanism for the building up of these resins from the polyhydric alcohol–polybasic acid reaction.

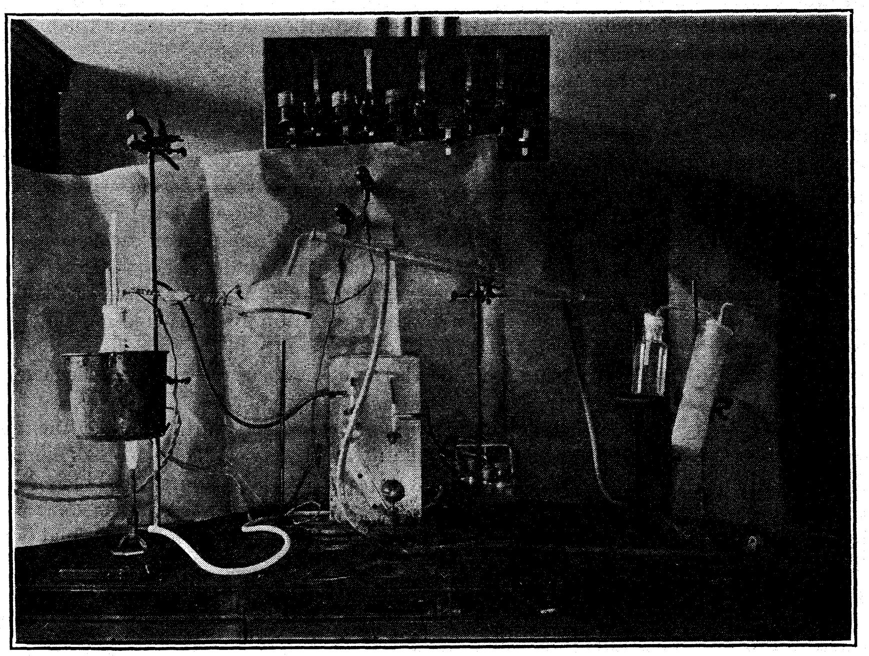


Fig. 1.

II. Kinetic Isothermal Studies of the Reaction **with** Time.—It would be extremely gratifying to be able to determine from time to time during the reaction the exact concentration not only of the phthalic anhydride and glycerol but also of the products, water and resin, as well. With such data the reaction velocities could be studied, and with the constants known it might be possible by comparison with data on the heat of reaction and specific heats to obtain free energy relationships for this unusual

---

[6] Barry, Drummond and Morell, "Natural and Synthetic Resins," D. Van Nostrand Co., New York, p. 164.

type of reaction. However, none of the standard methods for determination of glycerol or free hydroxyl groups has proved satisfactory. The determination of water content is tedious and uncertain; hence the reaction has been followed from the standpoint of free and combined acid.

Preparation of Samples.—The reaction has been followed by allowing it to proceed at atmospheric pressure, keeping it as nearly isothermal as possible, and by taking out samples from time to time. The theoretical proportion of glycerol, 184.2 g., was weighed out into the reaction vessel and warmed up to the temperature at which the reaction was to be carried out. At the same time phthalic anhydride was melted in an Erlenmeyer flask and raised slightly above the temperature at which the reaction was to take place, to allow for cooling when pouring. When it was desired to start the reaction, the molten phthalic anhydride was poured into the reaction vessel on the balance pan until the theoretical proportion, 444.2 g., was weighed out. The most accurate method of taking the time of the start of the reaction was when one-half of the molten anhydride had been poured in. As soon as the molten phthalic anhydride was added and stirred in, the temperature of the reaction mixture rose very rapidly above the point at which it was desired to run the reaction. Because the reaction was strongly exothermic at the start, it was necessary to cool as quickly as possible with a jet of compressed air, and the reaction vessel was not placed in the insulated oil-bath until the temperature was approximately that of the oil-bath. From then on it was necessary to supply heat to the reaction mixture in order to maintain isothermal conditions.

Samples were taken from time to time by pipetting out a small amount of the fluid into numbered containers; these were allowed to cool rapidly, thus freezing the equilibrium at that point. Samples were taken more frequently in the earlier stages of the reaction than in the latter stages, because the reaction was proceeding so much more rapidly.

The viscosity of the liquid reaction mixture kept increasing until suddenly the mass stiffened and became an irreversible gel. It was much more difficult to take samples after gelation. A heat of gelation might be expected, but no appreciable increase in temperature was noticed. A few samples were taken after the transition and some were left in an oven at 200° to react for a time, infinite in comparison, so that a final equilibrium value could be reached.

(a) **Free** Acidity.—The decrease in free acidity was determined and is reported both as percentage of free acidity, calculated as phthalic anhydride, and as acid value (acid number). The tared samples of about 1 g. each were dissolved in 25 cc. of C. P. acetone which had a low acidity "blank" and then titrated with standardized 0.1 *N* potassium hydroxide solution, using phenolphthalein as an indicator.

Table I shows the data obtained on the decrease of free acidity as the reaction proceeded. While this is as was expected, it is perhaps surprising to note that in every case the free acidity was reduced to approximately one-half within one minute after the start of the reaction. For the first instant the reaction is strongly exothermic. The temperature of the reaction mixture rapidly rises from 15 to 44° above the temperature of the substances when they were poured together. The data indicate that the reaction is about half way through at the end of the first minute, after which it proceeds at a greatly diminished rate until gelation occurs.

In Fig. 2 is plotted the decrease in free acidity with time. It is useful to report the acidity both as acid number and as percentage of free phthalic

TABLE I

ISOTHERMS OF FREE ACIDITY CHANGE WITH TIME

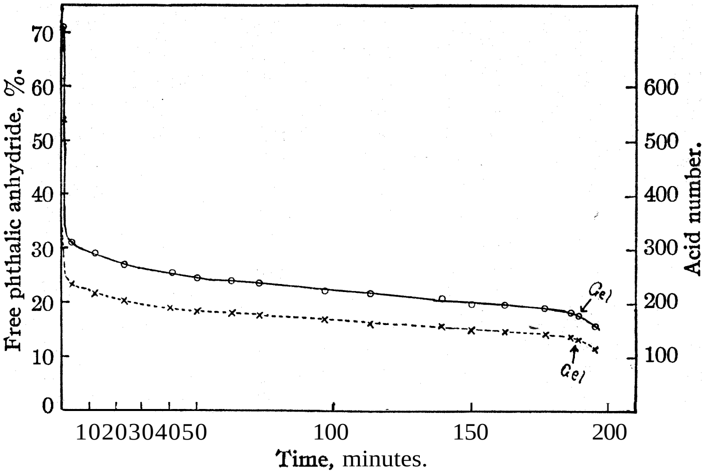
Time. sec.	Time, min.	Free anhydride, %	Add number	Time. sec.	Time, min.	Free anhydride, %	Acid number
	T = 195°				T = 215"		
0	0	70.67	535	0	0	70.67	535
215	3.58	31.05	235	45	0.75	34.96	264
720	32.16	28 99	218	150	2.50	32.52	246
1,320	23.0	27.02	212	320	5.33	30.46	231
2,440	40.67	25.25	191	575	9.58	27.67	210
3,420	50.0	24.51	185	1510	25.20	26.52	201
3,980	63.0	23.96	181	2175	36.25	24.55	186
4,380	73.0	23.42	177	2855	47 58	22 87	173
5,790	96.5	22.23	169	3855	64.25	20.28	154
6,780	113.0	21.47	163	5430	90.50	17.12	130
8,340	139 0	21.02	159	5520	92.00	15.60	118
9,000	150.0	19.93	151	5640$^+$	98.00	13.93	105
9,720	162 0	19.84	149	m	m	0.29	2.2
10,610	177.0	19.18	145		T = 230°		
11,150	186.0	18.31	139	0	0	70.67	535
11,340$^+$	189.0	17.94	136	15	0.25	40.85	318
11,700	195.0	15.81	119	190	3.20	37.98	288
	T = 200°			465	7.75	36.49	276
0	0	70.67	535	700	11.66	33.52	254
20	0.33	36.43	276	1625	27.08	27.24	206
60	1.00	33 86	256	2265	37.75	26.23	198
330	5.50	29.76	226	2505$^+$	41.55	16.87	127
630	10.50	28.25	214	2650	44.20	13.34	101
960	16.00	27.30	207	3465	57.75	11.86	90
1,455	24.25	25.55	194	m	m	1.32	10
1,935	32.25	24.26	184		T = 232°		
2,670	44.50	23.62	179	0	0	70.67	535
3,600	60.0	20.22	153	120	2.0	36.42	276
4,830	80.5	20.09	152	300	5.0	31.57	239
6,300	105.0	18.42	139	540	9.0	31.13	236
7,540	125.7	16.74	127	1050	17.5	27.89	211
9,060	151.0	16.25	123	1560	26.0	27.32	206
9,240$^+$	156.0	15.87	120	1860	31.0	24.63	187
9,720	162.0	13.71	108	2160	36.0	17.57	133
10,200	170.0	8.44	64	2220$^+$	37.0	15.72	109
140,400	2360.0	0.57	4.4				

$^+$ Indicates point where gelation took place.

anhydride. The curve illustrates clearly the sudden drop in free acid at the start of the reaction and the subsequent slow continuous change right up to gelation.

(b) Saponification Number.—If the resinous product is an ester, it should be saponifiable just as the less complex esters are. The saponification number should remain fairly constant unless affected by change in density of the resin or by volatilization of some free phthalic anhydride.

For the determination, 1-g. samples were refluxed in Erlenmeyer flasks for one hour with 50 cc. of N alcoholic potassium hydroxide solution. Upon cooling titration was made with 0.5 N hydrochloric acid until the pink color of phenolphthalein disappeared; 0.5 N potassium hydroxide solution then was run in until the pink color reappeared.



——, Free phthalic anhydride; - - - -, acid number.

Fig. 2.—Decrease of free acidity with time. T = 195°.

Fig. 3 shows how the saponification value remains fairly constant with time in contrast to the steady decrease in acid number.

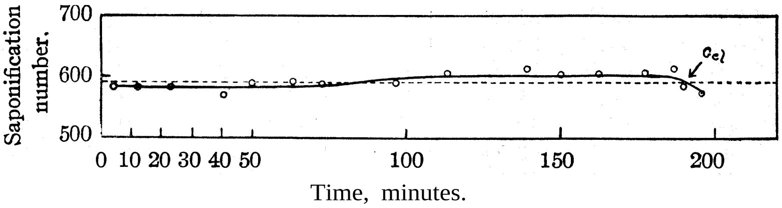


Fig. 3.—Variation of saponification number with time. T = 195°.

(c) **Degree of Esterification.**—The saponification number is useful in that it may be used to calculate the degree or percentage of esterification. When the acid number is subtracted from the saponification number, the resulting value is known as ester number or ester value, which represents the number of milligrams of potassium hydroxide equivalent to the acid which is combined in the ester.

$$\text{Ester number} = \text{saponification number} - \text{acid number}$$

$$\text{Percentage esterification} = \frac{\text{ester number}}{\text{saponification number}} \times 100 = \frac{(\text{saponification number} - \text{acid number})}{\text{saponification number}} \times 100$$

Fig. **4** shows how the percentage of esterification consistently increases with time. Analytical data show that various batches of glycerol–phthalic anhydride resin in manufacture have an esterification of 75–79% just before gelation.

(d) Variation of Other Properties with Time; **1. Flow Point.**—The change in flow point[7] with time was one of the earliest studies made in following the formation of the resinous condensate. The flow point[7] is that temperature at which a small sample of resin (0.50" thick) will flow under gravity a vertical distance of 0.20" when subjected to a gradual increase in temperature of 2–3° per minute. This value is correspondingly lower than the melting point but is more useful and may be more sharply determined. As the reaction proceeds, the flow point gradually increases until it reaches 115–118°, when gelation occurs. After gelation the resin flows only when pressure is applied. Fig. 5 shows the curve of increase of flow point with time.

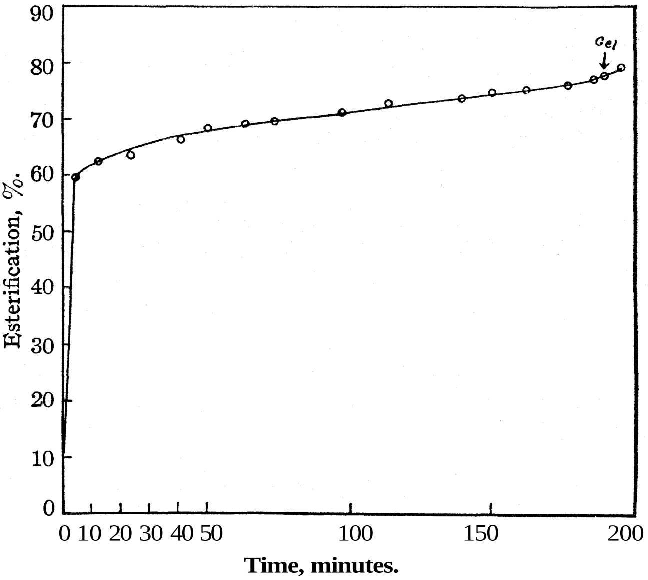


Fig. 4.—Increase of esterification with time. *T* = 195°.

2. Viscosity.—The viscosity of the liquid reaction mixture, which probably influences the flow point, has not been followed quantitatively. It is obvious that the viscosity is quite low at the start of the reaction, then gradually increases until at gelation it approaches an infinite value.

3. Density.—The density at 15.5/15.5°, as determined by a pycnometer with mineral oil for an insoluble liquid, was found to increase in the early stages of the reaction.

[7] **General Electric Standard** Test No. 24.

4. Color.—The color changes but slightly in going from a water white liquid to a very pale straw color at gelation.

5. **Refractive Index.—By** comparing the powdered resin with liquids of known refractive index, this value was found to change but slightly from 1.56 in the early stages of the reaction to 1.58 just before gelation.

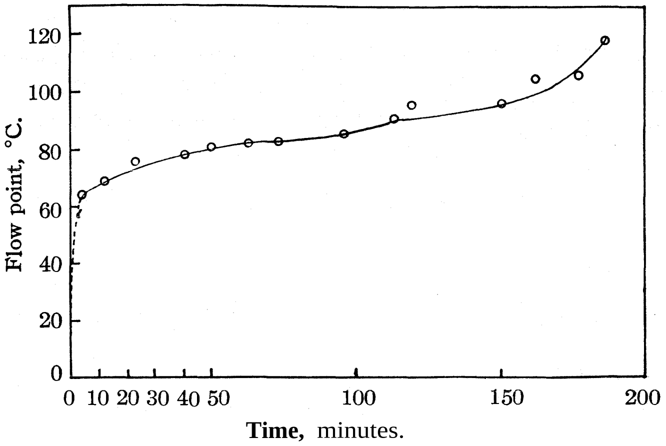


Fig. 5.—Increase of flow point with **time.** T = 195°.

Table II shows a comparison of the variation of the different properties of a set of standard samples taken from time to time, keeping the temperature at 195°.

TABLE II*a*

VARIATION OF PROPERTIES OF PRODUCTS WITH TIME AT 195°

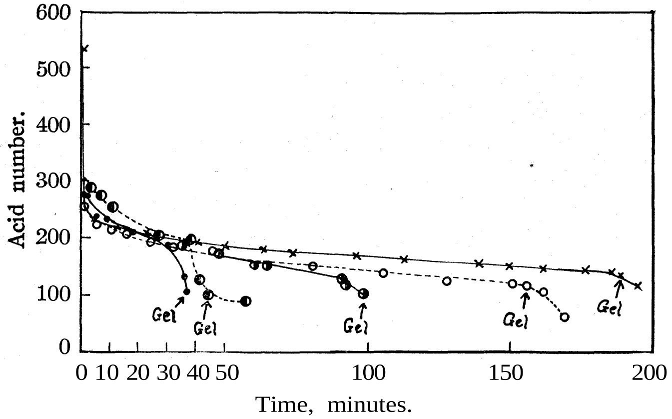
Time, sec.	Time. min.	Flow pt.. °C.	Refr. index	Acid number	Sapon. number	Ester value	Ester, %
0	0	...	..	(535)	...	0	0.0
215	3.58	64	..	235	584	349	59.8
720	12.16	69	..	218	582	364	62.5
1380	23.0	76	1.56	212	583	371	63.6
2440	40.67	78	..	191	570	379	66.5
3420	50.0	81	..	185	589	404	68.5
3980	63.0	82.5	..	181	591	410	69.4
4380	73.0	83	..	177	588	411	69.9
5740	96.5	86	..	169	589	420	71.4
6780	113.0	91	..	163	605	442	73.0
8340	139.0	96	..	159	611	452	73.8
9000	150.0	96	..	151	604	453	75.0
9720	162.0	105	..	149	605	456	75.5
10610	177.0	106	..	145	608	463	76.1
11150	186.0	118	1.58	139	614	475	77.3
11340	189.0	**Gel**	..	136	585	449	77.8
11700	195.0	Gel	..	119	574	455	79.3

TABLE II*b*

VARIATION OF PROPERTIES OF PRODUCTS WITH TIME AT 195°

Time sec.	$d^{15.5°}_{15.5°}$	Hot-plate cure of film at 275°, sec.	Color and consistency	Free phthalic anhydride, %
0	....	...	Mixture of molten components	70.67
215	....	282	Light color, sticky sirup	31.05
720	1.3323	233	Light, sticky balsam	28.99
1380	1.3644	212	Gummy and harder	27.02
2440	1.3687	183	......	25.25
3420	1.4232	163	Reaction mixture viscosity incr.	24.51
3980	....	141	Resin slightly darker	23.96
4380	....	113	Resin harder	23.42
5740	....	98	......	22.23
6780	....	82	......	21.47
8340	....	68	More brittle, less adhesive	21.02
9000	....	47	Water resistance increasing	19.93
9720	....	38	......	19.84
10610	....	28	Mixture still liquid (195°)	19.18
11150	....	16	Beginning to gel	18.31
11340	....	...	Real heat irreversible gel	17.94
11700	....	...	Leathery when hot, flows only with pressure	15.81

III. Effect of Temperature.—It is interesting to compare the isothermal curves by plotting the free acidity *vs.* time, Fig. 6. All of the curves are much the same for the early part of the reaction, but the isotherms obtained when the reaction was carried out at higher temperatures require shorter paths to reach gelation. This suggests a relationship between time of gelation and the temperature.



0,232°; ◐, 230°; ◑, 215°; O, 200°; X, 195°.

Fig. 6.—Isotherms of free acid *vs.* time, showing effect of temperature.

Fig. 7 shows that when gelation time is plotted against the reciprocal of the absolute temperature, the result is a straight line.

Discussion

The data indicate that as the glycerol–phthalic anhydride reaction proceeds, the changes in the various properties are gradual and continuous. This makes it rather doubtful whether the reaction takes place in certain steps, such as the formation first of a monoglyceride, then a diglyceride and finally a triglyceride. It is more likely that a heterogeneous complexity of esters results, and finally the formation of more complex structures.

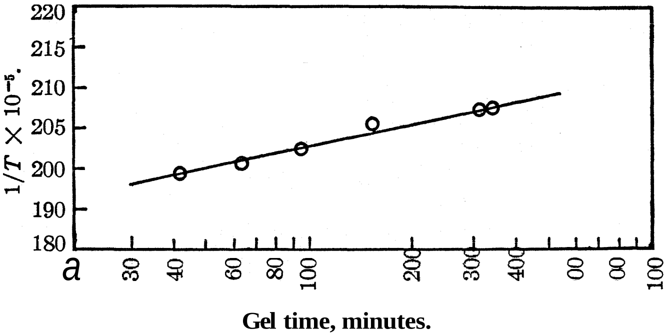


Fig. 7.—Gel time *vs.* reciprocal of absolute temperature.

Increase in temperature promotes the rapidity of this reaction, as in the case of the simpler esters. Regardless of the temperature at which this reaction is carried out, it does not seem possible to carry this reaction to completion, since gelation (with obstruction to mobility) invariably occurs between 75–79% esterification.

In the study of this resin-producing reaction, no evidence was found to indicate that anything but simple esterification occurred. This fact, together with the others just mentioned, must be taken into account in any theory of resinification, which is a problem that the authors hope in the near future to discuss in detail.

Summary

1. The glycerol–phthalic anhydride reaction proceeds by esterification, since water was the only product collected. No intermediate aldehyde was detected until near gelation.

2. The reaction went very rapidly at the start, evolving heat, and was apparently about one-half complete within one minute.

3. As the reaction proceeded under isothermal conditions, the free acidity decreased, the saponification number remained fairly constant and the percentage of esterification increased. The changes in other properties with time were noted.

4. Similar resinous products result if other polyhydric alcohols are substituted for glycerol, or if other polybasic acids are substituted for phthalic anhydride.

5. At whatever temperature the glycerol–phthalic anhydride reaction is carried out, gelation occurs before the esterification has an opportunity to complete itself.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

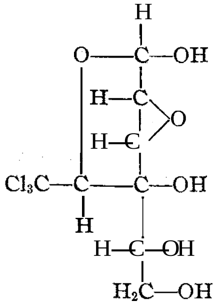
STRUCTURE OF BETA-GLUCOCHLORALOSE[1]

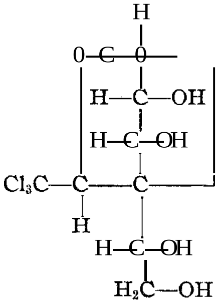
BY H. W. COLES, L. D. GOODHUE AND R. M. HIXON

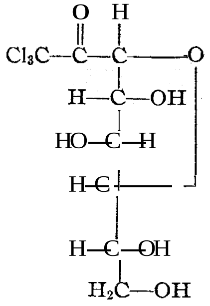
RECEIVED SEPTEMBER 24, 1928 PUBLISHED FEBRUARY 5, 1929

Two crystalline chloral derivatives of glucose were reported by Heffter[2] in 1889 but were not named. More detailed studies of the chloral derivatives of the various carbohydrates have been made by Hanriot[3] and his associates, by Meunier,[4] by Petit and Polonowski,[5] and by Pictet and Reichel.[6] The most recent formula for the β-glucochloralose is that of Pictet and Reichel (Formula III). Most of the standard handbooks give the older formula of Hanriot (Formula I) or of Polonomski (Formula II).

The evidence regarding the structure of β-glucochloralose is conflicting. The absence of reducing properties, the failure to combine with hydroxylamine and phenylhydrazine and the resistance of the compound to hydrogenation all indicate that the free aldehyde groups of both the glucose and the chloral have been modified in their union. The formation of


I


II


III

---

[1] This compound is also called "Parachloralose."

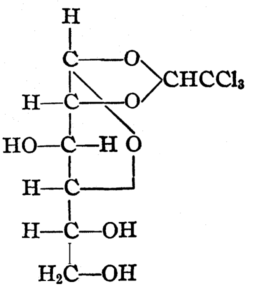
[2] Heffter, *Ber.*, 22, 1050 (1889).

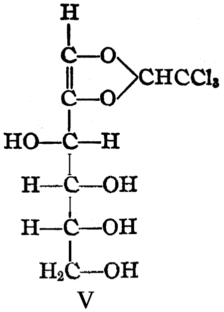
[3] Hanriot and Richet, *Compt. rend.*, 116, 63 (1892); 117, 734 (1893); 122, 1127 (1896); *Bull. soc. chim.* [3], 9, 947 (1893); [3], 11, 37, 258, 303 (1894); Hanriot, Ann. *chim. phys.*, 18, *466* (1909); Hanriot and Kling, *Compt. vend.*, 152, 1398, 1596 (1911); 156, 1380 (1913).

[4] Meunier, *Ann. chim. phys.*, [6] 22, 413 (1906).

[5] Petit *and* Polonowski, *Bull. soc. chim.*, [3] 11, 125 (1894).

[6] Pictet and Reichel, Hek. *Chim. Acta,* 6, 621 (1923).


IV


V

Formulas for p-glucochloralose.

tetra-derivatives and the fact that the carbohydrate chain can be oxidized by nitric acid without rupture of the glucose–chloral linkage have been used as evidence for the above formulas. The essential points which these formulas depict are: (a) a carbon–carbon linkage between the chloral and glucose radicals and (b) the presence of four free hydroxy groups.

On the other hand, the chloral condensation products with glycerin' and with the α-hydroxy acids[8] have been considered to have acetal linkages analogous to the other aldehyde and ketone condensation products with the poly-alcohols. Similar structures are also assumed to be present in the dichloral glucoses.[9] The reaction reported by Hanriot and Kling[10] would be highly indicative that this is also the case in β-glucochloralose. The reaction was accordingly duplicated for confirmation. β-Glucochloralose was reduced by means of aluminum amalgam to dechloro-β-glucochloralose (glucose-dichloroacetaldehyde). This compound was hydrolyzed by refluxing with dilute hydrochloric acid. The dichloro-acetaldehyde was distilled out and converted to both the oxime and osazone of glyoxal for identification. The glucose was isolated as the osazone. It seems improbable that the removal of one chlorine atom would render the linkage shown in either Formula I, II or III as labile as this reaction would indicate.

The conversion of β-glucochloralose to two different dichloralglucoses identical with those previously reported in the literature would appear to harmonize with only this acetal type of structure. There would appear to be no logical explanation for the condensation of chloral with β-glucochloralose as represented by any of the proposed formulas containing four free hydroxy groups, to give a dichloralglucose containing but one free hydroxy group. The only formula that suggests itself as being in harmony with these facts is an acetal type of linkage in the p-glucochloralose,

---

[7] Yoder, This Journal, 45,475 (1923).

[8] Boeseken, *Verslag Akad. Wetenschappen Amsterdam,* 35, 1084 (1926).

[9] Ross and Payne, This Journal, 45,2363 (1923).

[10] Hanriot and Kling, *Bull. soc. chim.,* [4] 11,207 (1912).

with a keto-enol isomerization similar to that shown in Formulas IV and V to explain the formation of tetra-derivatives.

The linkage shown in IV is that of the 1,2-monochloralglucose. This structure presumably belongs to the compound reported in this paper as being formed by the condensation of chloral with 3,5,6-trimethylglucose obtained from the corresponding mono-acetone glucose. This compound is not identical with the trimethyl-β-glucochloralose obtained by direct methylation of β-glucochloralose. The two isomeric trimethylchloralglucoses are very similar in solubilities. The 3,5,6-trimethylmonochloralglucose gives no reaction for an active hydrogen with the Zerewitinoff test.[11] The trimethyl-β-glucochloralose not only gives this test but forms a monoacetyl derivative.[12]

Evidence regarding the positions of the methyl groups in trimethyl-β-glucochloralose was sought by removing both one and two of the chlorine atoms and hydrolyzing the reduced chloral group to give the free trimethylglucose. The dichloro-acetaldehyde was easily characterized by its oxime and osazone but sufficient monochloro-acetaldehyde was not obtained to be certain of its identity. In both derivatives the strength of acid necessary to hydrolyze the compounds was so strong (about 1 N) that partial decomposition of the methylated sugar resulted. The impure sirup obtained by vacuum distillation resembled the 3,5,6-trimethylglucose in its instability toward acids and in being levorotatory.

Experimental Part

Preparation of β-Glucochloralose.—The following method of preparation of β-glucochloralose was found most satisfactory: 300 g. of chloral hydrate and 400 cc. of concd. sulfuric acid are cooled in running water to 12–15°. As soon as the chloral layer begins to separate, 200 g. of glucose is stirred in using a strong mechanical stirring apparatus, the blades of which should be near the bottom of the beaker to prevent clogging with the floating cakes of material. After stirring for ten to twelve hours at 12–15°, the reddish, viscous mass, which should show no evidence of charring, is poured slowly with violent stirring into 4 liters of cold water. The white precipitate of dichloralglucoses is allowed to settle. The mother liquor is decanted, brought to a boil and allowed to cool slowly. The β-glucochloralose which separates at this point is recrystallized from alcohol, several recrystallizations being necessary for absolute purity; yield, 60 g.

Separation of the Dichloralglucoses.—The precipitate of dichloralglucoses obtained in the above procedure is heated with 500 cc. of water and small portions of sodium hydroxide are added until the excess chloral is driven off and the mixture becomes slightly alkaline. The crude product is filtered off and washed; yield, about 100 g.

A hot alcoholic extract of this product yields the dichloralglucose of m. p. 225° frequently reported in the literature. Only one recrystallization is necessary for purification.

---

[11] Zerewitinoff, Ber., 40,2023 (1907); *Z. anal. Chem.*, 68,321 (1926).

[12] This compound will be reported in a later paper. Attempts to introduce a fourth methyl group have as yet proved negative.

Evaporation of the alcoholic mother liquor leaves a sirup which is taken up in hot carbon tetrachloride and filtered from insoluble materials. Cooling and concentrating this solution yields the dichloralglucose, m. p. 135°, frequently described in the literature. The yield of the two dichloralglucoses is about equal.

It is possible that other dichloralglucoses can be isolated from this mixture, as further information regarding their specific solubilities becomes available. At times a compound of m. p. 188° is obtained with the latter fraction mentioned above.

Conversion of β-Glucochloralose into Two Different Dichloralglucoses.—Twenty g. of β-glucochloralose was treated with 100 g. of chloral hydrate and 100 cc. of sulfuric acid as described for glucose. After the precipitation with water and washing free from acid as in the previous directions, the dichloralglucoses were separated from the unchanged compound by taking up in acetone. The mixture of the two dichloralglucoses is thrown out of the acetone as a white powder by adding water until it is turbid and allowing to stand for two or three hours. The powder (about 10 g.) is dried at 70° until the odor of chloral is no longer noticeable and is then extracted with 200 cc. of hot benzene.

One of the dichloralglucoses (m. p. 268°) is insoluble in benzene and remains as a residue (about 3 g.). Acetylation yielded the mono-acetate (m. p. 198°) as reported by Ross and Payne.[9] Both of these compounds were also checked by chlorine analysis.

Slow evaporation of the benzene solution yields about 6 g. of an isomeric dichloralglucose (m. p. 225°). This compound was checked by a mixed melting point with the dichloralglucose isolated as a by-product in the preparation of the β-glucochloralose. Acetylation yielded the mono-acetate (m. p. 126°), as reported by Ross and Payne.[9]

Trimethyl-β-Glucochloralose.—It was found impossible to methylate β-glucochloralose by either the silver oxide method of Purdie and Irvine[13] or by the original dimethyl sulfate reaction proposed by Haworth.[14] The following modification of the latter method was found quite successful: 5 to 7 g. of finely powdered β-glucochloralose is placed in a three-necked flask provided with a condenser and a mercury-sealed mechanical stirrer; 100 cc. of dimethyl sulfate is added and the mixture is warmed to 60° until nearly all of the compound is in solution. The water-bath is removed and 25 g. of sodium hydroxide in pieces the size of a pea is added. If the mixture is kept dry the reaction is slow but as the reaction proceeds it becomes more rapid and care must be taken to prevent too high temperature. The excess dimethyl sulfate is destroyed by adding sodium hydroxide in 3 g. portions until the reaction mixture becomes basic. Small amounts of water are added as the mixture becomes too thick to stir.

The reaction mixture is extracted repeatedly with chloroform, the chloroform extract concentrated to a sirup, the sirup taken up in methyl alcohol and crystallized by careful addition of water; yield, 4 g. After recrystallization from petroleum ether the melting point remains constant at 109–110°.

Anal. (Carius). Calcd. for $C_{11}H_{17}O_6Cl_3$: Cl, 30.28. Found: Cl, 30.44, 30.42.

The trimethyl-β-glucochloralose showed little or no rotation in methyl alcohol (concd. 2.2% in a decimeter tube). The crystals are soluble in hot water, glacial acetic acid and ethyl acetate. Repeated methylation by the above method did not change the compound.

Trimethyl Monodechloro-β-glucochloralose (Trimethylglucose-dichloro-acetaldehyde).—Seven g. of trimethyl-β-glucochloralose was dissolved in 250 cc. of alcohol containing 5 cc. of concd. hydrochloric acid. The solution was diluted with water until precipitation just began. This solution is held at 50–60° under reflux for twenty-four

---

[13] Purdie and Irvine, J. *Chem. Soc.*, 83, 1021 (1903); 85, 1049 (1904).

[14] Haworth, *ibid.*, 107, 8 (1915).

hours while an excess of aluminum amalgam is added in small portions. If the amalgam is added in one portion, it tends to become inactive. As the reaction becomes alkaline, acid is added. The alcohol is distilled out under reduced pressure and the residue is extracted with ether. The oil obtained from the ether is difficult to obtain crystalline, the best method being to precipitate it carefully from alcoholic solution by slowly adding water; m. p. 68°; yield, 3 g.

Anal. Calcd. for $C_{11}H_{18}O_6Cl_2$: C, 41.63; H, 5.72; Cl, 22.37. Found: C, 41.78, H, 5.75; Cl, 22.33, 22.57.

Acid hydrolysis of 5 g. of this compound in 30 cc. of water and 7 cc. of hydrochloric acid (concd.) at boiling temperatures under reflux for six hours yielded positive tests for the dichloro-acetaldehyde (osazone of glyoxal) but the sugar resinified.

Lower concentrations of acid caused only slight hydrolysis. Several attempts were made to purify the methylated sugar by vacuum distillation but in no case was it possible to free the sirup from chlorine. The sirup was slightly levorotatory.

Trimethylbidechloro-β-glucochloralose (Trimethylglucose Monochloro-acetaldehyde).—The trimethyl-β-glucochloralose was reduced with sodium amalgam under various conditions. The reduced compounds would not crystallize so they were subjected to vacuum distillation. A clear sirup which partially crystallized came over at 155–160° (bath temp.) under 4 mm. The chlorine analysis was slightly low for the monochloro compound (calcd., 12.8; found, 11.72). Hydrolysis of the sirup yielded results similar to those described for the preceding compound.

Mono-acetone glucose has been prepared by partial hydrolysis of diacetoneglucose in water solutions.[15] A more convenient method has been found by taking advantage of the insolubility of the mono-acetoneglucose in ethyl acetate as compared to the solubility of the diacetoneglucose. Fifty g. of diacetoneglucose is dissolved in 400 cc. of ethyl acetate containing 4 cc. of concentrated nitric acid. The solution is heated to boiling and then cooled. The mono-acetoneglucose separates at once and is pure after one recrystallization from either water or neutral ethyl acetate.

3,5,6-Trimethylmonochloralglucose.—Five g. of 3,5,6-trimethylglucose, prepared from mono-acetoneglucose, was added to 40 cc. of sulfuric acid and 30 g. of chloral hydrate cooled in an ice-bath and mechanically stirred. After four hours the solution was stirred into 400 cc. of ice water. The separated gummy mass was taken up in chloroform and washed with sodium hydroxide solution to free it from sulfuric acid. After the evaporation of the chloroform the sirup was allowed to crystallize from alcohol and was then recrystallized from petroleum ether. The melting point gradually changed from 109 to 120° after many recrystallizations; yield, 2 g.

Anal. Calcd. for $C_{11}H_{17}O_6Cl_3$: Cl, 30.28. Found: Cl, 30.54. Rotation. Soln. 0.8413 g.; chloroform, 9.998 cc. (by wt.). $\alpha_D^{25} = -2.44°$ in a decimeter tube; $[\alpha]_D^{25} = -29.01°$.

The compound does not react with methylmagnesium iodide, which would indicate the absence of free hydroxyl groups. The solubilities are about the same as for the isomeric compound obtained by methylation of β-glucochloralose.

Summary

1. Trimethyl-β-glucochloralose is reported from the methylation of β-glucochloralose. Attempts to introduce a fourth methyl group have proved negative although an acetyl group can be introduced.

2. 3,5,6-Trimethylmonochloralglucose is reported from the condensation of chloral with 3,5,6-trimethylglucose.

---

[15] Irvine and Macdonald, *J. Chem. Soc.*, 107, 1701 (1915).

3. β-Glucochloralose condenses with chloral to yield two dichloralglucoses identical with those previously reported in the literature.

4. It is pointed out that the present formulas for β-glucochloralose cannot explain the formation of the dichloralglucoses. The reaction reported by Hanriot and Kling by which both the aldehyde and glucose are identified would indicate an acetal rather than a carbon–carbon linkage.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

ORIENTATION IN THE BENZENE RING. THE BROMINATION OF 2-AMINORESORCINOL DIMETHYL ETHER[1]

BY ARTHUR A. LEVINE AND HOOPER LINFORD

RECEIVED SEPTEMBER 25, 1928 PUBLISHED FEBRUARY 5, 1929

It has been shown in preceding papers[2] that the 2,6-dimethyl ether of pyrogallol gives on halogenation in an anhydrous medium a monohalogen substitution product in which the halogen atom has substituted meta to the hydroxyl group. The bromination of 2-aminoresorcinol dimethyl ether, which has an analogous structure, has been investigated in order to determine the mechanism of the reaction. Two courses are open for the entering halogen atom, it may substitute directly in the ring or else replace one of the amino hydrogens and subsequently migrate to the ortho-ortho-para positions as shown by Chattaway and Orton[3] in case of acetanilide. It may be assumed that in 2-aminoresorcinol the bromine atom enters the amino group and subsequently migrates to the para position, but such is not the case, apparently, since the product obtained has the bromine atom in the meta position to the amino group. It has not been possible to prepare the N-bromo derivative and actually determine whether the bromine atom migrates to the meta position. Every effort gave oxidation products.

The acetanilide of 2-aminoresorcinol dimethyl ether was brominated with a calculated quantity of bromine in acetic acid as a solvent. Numerous attempts have been made to brominate the free base in an anhydrous medium. Satisfactory results have been obtained on bromination of the free base in glacial acetic acid containing a small quantity of acetic anhydride. The product obtained, however, was the corresponding monobromo-acetanilide. The formation of the acetanilide is rather unusual, taking place with the utmost ease at room temperature, while Kauffmann

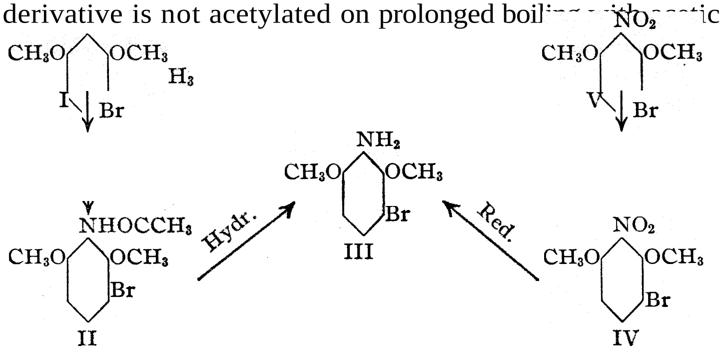
---

[1] Abstracted from a thesis by Hooper Linford, presented to the Graduate Faculty of the State College of Washington in partial fulfilment of the requirements for the degree of Master of Science.

[2] (a) Levine, THIS JOURNAL, 48, 2719 (1926); (b) 49, 797 (1927).

[3] Chattaway and Orton, Ber., 32, 3573, 3635 (1899).

and Franck[4] found that 2-aminoresorcinol dimethyl ether acetylates with difficulty. It has also been found in this Laboratory that the monobromo derivative is not acetylated on prolonged boiling with acetic anhydride,



Determination of the Position of the Bromine Atom.—The bromoacetanilide (II) was hydrolyzed with alcoholic potassium hydroxide, giving the free base (III). This was compared and found identical with the compound (IV) obtained on bromination of 2-nitroresorcinol dimethyl ether (V) and subsequent reduction of this bromoderivative. It is assumed that the bromine atom enters into the ring in the meta position to the nitro group since the combined effect of the groups already present orient in that position. Efforts to oxidize the bromo derivative to the corresponding quinone have not yielded the desired product, complex oxidation products containing nitrogen being obtained. Likewise, attempts to diazotize and convert the brominated amine to the corresponding phenol, 3-bromo-2,6-dimethyl ether of pyrogallol, whose constitution has been established,[2b] have not been possible.

Experimental Part

Preparation of **2-Aminoresorcinol Dimethyl** Ether.—This was prepared by the method of Kauffmann and Franck.[4] It was used without any further purification in the preparation of the acetanilide and in subsequent brominating experiments.

The acetanilide of 2-aminoresorcinol dimethyl ether was prepared by heating 5 g. of the free base with 50 cc. of freshly distilled acetic anhydride in a sealed tube for about four hours at a temperature of 150–160". If the heating is continued for about ten hours, as recommended by Kauffmann and Franck, the chief product is not the acetanilide but a substance melting at 181°. This substance will be described in a subsequent paper.

Bromination of the Acetanilide of 2-Aminoresorcinol Dimethyl Ether.—Five grams of the acetanilide was dissolved in 50 cc. of glacial acetic acid and 4.5 g. of bromine dissolved in 15 cc. of acetic acid was added. The bromination occurred readily with evolution of hydrogen bromide. After standing for one-half hour the reaction mixture was poured into 300 cc. of water. A precipitate formed, which was filtered off and on crystallization from the glacial acetic acid two substances were obtained, a monobromo derivative melting at 161–162°, and a dibromo derivative melting at 212–213°.

---

[4] Rauffmann and Franck, *Ber.,* 40, 4006 (1907).

Bromination of the Acetanilide with Four Equivalents of Bromine.—Five grams of the acetanilide dissolved in 50 cc. of acetic acid was treated with 9 g. of bromine dissolved in 15 cc. of acetic acid; on pouring the reaction mixture into water and crystallizing the product from acetic acid, a substance identical with the one above melting at 212–213° was obtained as the only product that could be isolated. If the bromination was carried out at the temperature of the steam-bath, either with four equivalents or an excess of bromine, a product melting at 187–188° was formed. This is a dibromo derivative isomeric with the one melting at 213–214°.

Bromination of the Free Base in Glacial Acetic Acid in the Presence of Acetic Anhydride.—To five grams of 2-aminoresorcinol dimethyl ether dissolved in 50 cc. of acetic anhydride was added 5.1 g. of bromine, in 10 cc. of glacial acetic acid. After one hour the resulting mixture was poured into 200 cc. of water. The precipitate was filtered off and recrystallized from alcohol. This product, melting at 161–162°, was identical with the bromo-acetanilide obtained above. If an excess of bromine was used and the reaction carried out at the temperature of the steam-bath, a product identical with the substance melting at 187–188° was obtained as the sole product.

The **Acetanilide** of **4-Bromo-2-aminoresorcinol Dimethyl** Ether.—This was obtained on bromination of the acetanilide of 2-aminoresorcinol dimethyl ether or the free base. It was purified by repeated recrystallization from dilute acetic acid and subsequently from benzene until a constant melting point was obtained. From the former solvent it crystallized in hexagonal plates and from the latter in fine needles. It is soluble in alcohol, acetic acid, benzene and ether but insoluble in water and ligroin. It melts at 161–162°.

Anal. Subs., 0.2090, 0.2140: CO_2, 0.3320, 0.3424; H_2O, 0.0830, 0.0847. Subs., 0.2191. 0.2304: AgBr, 0.1528, 0.1610. Calcd. for $C_{10}H_{12}O_3NBr$: C, 43, 80; H, 4.41; Br, 29.70. Found: C, 43.34, 43.65; H, 4.44, 4.43; Br, 29.68, 29.74.

Hydrolysis of the **Acetanilide.**—Four grams of the above acetanilide was refluxed for two hours with 200 cc. of 2 *N* alcoholic solution of potassium hydroxide. The reaction mixture was acidified with hydrochloric acid and extracted with ether, yielding a small quantity of the original substance melting at 161–162°. The acid solution was made alkaline with sodium hydroxide and extracted with ether. The ethereal extract was dried with anhydrous sodium sulfate and on evaporation gave an oily product (3 g.) which solidified on cooling.

4-Bromo-2-aminoresorcinol dimethyl ether obtained as described above was crystallized from alcohol, forming small scale-like crystals melting at 67–68°. It is quite soluble in the usual organic solvents.

Anal. Subs., 0.0982, 0.1769: AgBr, 0.0785, 0.1426. Calod. for $C_8H_{10}O_2NBr$: Br, 34.44. Found: 34.27, 34.41.

Reduction of **4-Bromo-2-nitroresorcinol Dimethyl** Ether.—Ten grams of 4-bromo-2-nitroresorcinol dimethyl ether prepared by the method of Kauffmann and Franck[5] was refluxed with 15 g. of tin and 50 cc. of concentrated hydrochloric acid for one hour. On cooling enough water was added to keep the tin double salt in solution and enough potassium hydroxide added to make the solution strongly alkaline. The solution was extracted three times with ether and the ether extract was dried with anhydrous sodium sulfate. After evaporation of the ether an oily residue remained which solidified when cold. It was crystallized from alcohol and found to be identical with the bromo-2-aminoresorcinol dimethyl ether obtained on hydrolysis of the acetanilide described above.

Attempts have been made to prepare the acetanilide of 4-bromo-2-aminoresorcinol

---

[5] Ref. 4, p. 4002.

dimethyl ether by refluxing the free base obtained above with acetic anhydride; this has not been possible. The product obtained had lost a methoxy group. This will be discussed further in a subsequent paper.

The Acetanilide of Dibromo-2-aminoresorcinol Dimethyl Ether Melting at 213–214°.—This was obtained by bromination of the acetanilide or the free base in acetic acid and acetic anhydride as described above. It was repeatedly recrystallized from alcohol and subsequently from benzene, forming fine white needle-like crystals.

Anal. Subs., 0.1039: AgBr, 0.1087. Calcd. for $C_{10}H_{11}O_3NBr_2$: Br, 45.15. Found: Br, 45.52.

The isomeric dibromo derivative melting at 187–188° was obtained by brominating the acetanilide of 2-aminoresorcinol dimethyl ether at the temperature of the steam-bath. It was crystallized from benzene.

Anal. Subs., 0.1104: AgBr, 0.1175. Calcd. for $C_{10}H_{11}NBr_2$: Br, 45.15. Found: Br, 45.30.

Summary

It has been shown that the bromine atom enters the meta position to the amino group in 2-aminoresorcinol dimethyl ether.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE DERMATOLOGICAL RESEARCH LABORATORIES]

DERIVATIVES OF MONO- AND DIAMINOHYDROXYPHENYLARSONIC ACIDS

BY BARRETT C. FISHER AND GEORGE W. RAIZISS

RECEIVED SEPTEMBER 27, 1928 PUBLISHED FEBRUARY 5, 1929

The practical significance of 3-amino-4-hydroxyphenylarsonic acid lies in its chemical relationship to such valuable medicinal products as arsphenamine and its derivatives, as well as stovarsol (acetarsone). The first is produced by reduction of 3-amino-4-hydroxyphenylarsonic acid, while the latter is the N-acetyl derivative of the same acid. Recent investigations indicate that 3-amino-4-hydroxyphenylarsonic acid itself is valuable in the treatment of protozoan infections.[1] The purpose of this paper is to describe several new derivatives of the above acid and also of the closely related diaminohydroxyphenylarsonicacid, all of which were synthesized by us in the course of chemotherapeutic research.

Of the halogenated 3-amino-4-hydroxyphenylarsonic acids, the 5-chloro[2] and 5-iodo[3] derivatives are known. We succeeded in preparing 5-bromo-3-amino-4-hydroxyphenylarsonic acid by first brominating the corresponding nitrohydroxyarsonic acid and then reducing the resulting product to the amino derivative. The direct bromination of 3-amino-4-

[1] Levaditi and Navarro-Martin, *Compt. rend. acad. sci.*, 174, 893 (1922); Fourneau, Navarro-Martin and Mr. and Mrs. Trefouel, *Ann. inst. Pasteur*, *37*, 551 (1923); Petzetakis, *Presse Medicale*, March 7, 1925.

[2] Benda and Schmidt, U. S. Patent 1,595,498 (1926).

[3] Macallum, J. *Chem. Soc.*, 1645 (1926); Maschmann, *Ber.*, 59B, 213 (1926).

hydroxyphenylarsonic acid could not be effected because of the readiness with which the amino acid oxidizes. The bromo-amino product can be obtained in even purer form than its parent amino compound, because it is more stable and crystallizes readily from water in beautiful colorless prisms. We assume that in brominating, as in mercurating, 3-nitro-4-hydroxyphenylarsonic acid the halogen, like mercury, enters position 5 of the benzene ring.[4] Most of the chemical properties and solubilities of 5-bromo-3-amino-4-hydroxylphenylarsonic acid are identical with those of the parent compound (3-amino-4-hydroxyphenylarsonic acid) except that it is soluble in hot water. It reacts with acetic anhydride, forming the corresponding acetyl compound, which is particularly interesting because it is a bromo derivative of the pharmaceutically important 3-acetylamino-4-hydroxyphenylarsonic acid (acetarsone). The halogenated compound, however, is more soluble in water.

3,5-Diamino-4-hydroxyphenylarsonic acid can now be produced with good yields due to improvements in the method of preparation. In a previous article[6] the fact that this compound crystallizes with $^1/_2$ molecule of water was overlooked, so that the analytical results now more closely approximate the theoretical figure. N-acyl derivatives of the 3,5-diamino acid are formed with comparative ease; the formyl compound is obtained at ordinary temperature after twenty-four hours, while the other acyl derivatives result within ten to fifteen minutes. In all cases substitution occurred in both amino groups. Of particular interest is 3,5-di-(chloro-acetylamino)-4-hydroxyphenylarsonic acid; it possesses the property of combining with one molecule of an amine, forming the corresponding mono glycyl derivative of the type formula, $C_6H_2(AsO_3H_2)$-$(OH)(NHCOCH_2Cl)(NHCOCH_2HNR)$. These will be described in a subsequent paper.

3-Acetylamino-4-hydroxyphenylarsonic acid is utilized in therapy as such. We prepared various salts of this acid in order to ascertain whether or not they possess any therapeutic advantages over the parent compound. The alkali salts are soluble in water, while the alkaline earth salts, except that of strontium, are insoluble. They all crystallize with water of crystallization; the only exceptions are the strontium and barium salts.

5-Bromo-3-amino-4-hydroxyphenylarsonic acid, as well as its N-acyl and diacyl derivatives, are not more trypanocidal or spirocheticidal than 3-amino-4-hydroxyphenylarsonic acid itself or its acetyl derivative. The least toxic of all the compounds described in this paper is 3,5-di-(acetylamino)-4-hydroxyphenylarsonic acid. Its maximum tolerated dose for white rats by the intravenous route is 1.4 g. per kilogram of body weight; for rabbits, 0.6 g. per kilo. These figures appear more significant when

---

[4] Stieglitz, Kharasch and Hanke, THIS JOURNAL, 43, 1185 (1921).

[5] Raiziss and Gavron, *ibid.*, 43, 583 (1921).

compared with those obtained for 3-acetylamino-4-hydroxyphenylarsonic acid under the same conditions, *viz.*, 0.3 g. per kilo for rats.

Experimental Part

Salts of **3-Acetylamino-4-hydroxyphenylarsonic** Acid.—The lithium salt, $Li_2O_3As\cdot C_6H_3(OH)(NHOCCH_3)\cdot 2H_2O$, is prepared by suspending 1 mole of 3-acetylamino-4-hydroxyphenylarsonic acid in a small volume of water, heating to boiling, gradually adding 2 moles of lithium carbonate and heating until the evolution of carbon dioxide ceases. After filtering and cooling, the filtrate is treated with 10 volumes of acetone and the lithium salt separates out immediately. This is filtered off and washed first with acetone and then ether. It is a colorless, amorphous powder soluble in water, methyl and ethyl alcohols; it is insoluble in acetone or ether.

The calcium and barium salts, $CaO_3As\cdot C_6H_3(OH)(NHOCCH_3)\cdot 2H_2O$ and $BaO_3As\text{-}C_6H_3(OH)(NHOCCH_3)$, are prepared like the lithium salt except (1) that the parent arsonic acid is suspended in 50 parts of water, (2) the reaction mixture is boiled for twenty minutes and (3) the salts crystallize out spontaneously from the filtrate when cooled to 15°, without the aid of a prtcipitant. They are washed successively with water, methyl alcohol and ether, and finally air dried. The calcium salt crystallizes in colorless, highly refractive crystals, while the barium compound exists as colorless needles. They are both soluble in hot water but only sparingly so in cold; they are insoluble in methyl or ethyl alcohol, acetone or ether.

The strontium salt, $SrO_3AsC_6H_3(OH)(NHOCCH_3)$, is prepared like the lithium salt except that it is precipitated from the filtrate at 10° with 3 volumes of 95% methyl alcohol. It is allowed to stand at 10° for one hour, then filtered off and washed first with methyl alcohol and ultimately with ether. It forms colorless rhombohedra which are very soluble in cold water but insoluble in organic solvents.

TABLE I

ANALYTICAL DATA

Salt of	Nitrogen, % Calcd.	Nitrogen, % Found	Arsenic. % Calcd.	Arsenic. % Found
Lithium	4.33	4.48	23.23	23.58
Calcium	4.01	4.05	21.48	21.95
Barium	3.41	3.31	18.29	18.79
Strontium	3.88	4.05	20.79	21.39

Bromo Derivatives of Aryl Arsonic Acids

5-Bromo-3-nitro-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2BrNO_2OH$.—263 g. (1 mole) of 3-nitro-4-hydroxyphenylarsonic acid is suspended in 800 cc. of 95% methyl alcohol, 20 g. of iron added (as a carrier), the flask connected to a reflux condenser and a solution of 160 g. of bromine in 200 cc. of methyl alcohol introduced drop by drop, with frequent shaking. The reaction must not to be permitted to become too violent. After all of the bromine has been added, the reaction mixture is cooled, filtered and the filtrate treated with 10 volumes of water. The yellow bromo derivative precipitates immediately; it is washed with water and then crystallized from the same medium; yield of recrystallized product, 154 *g.*

5-Bromo-3-nitro-4-hydroxyphenylarsonic acid crystallizes in yellow, microscopic plates which are soluble in hot water, but almost insoluble in cold, sparingly soluble in dilute hydrochloric acid, readily in dilute alkalies, acetone, ethyl or methyl alcohol, insoluble in ether and most other organic solvents. When heated it starts to decompose at about 280°, but remains unmelted at 300°.

Anal. Calcd. for $C_6H_5O_6NAsBr$: N, 4.08; As, 21.93. Found: N, 3.63; As, 21.46.

5-Bromo-3-amino-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2BrNH_2OH$.—Thirty-four and two-tenths g. of the corresponding nitro compound is dissolved in 50 cc. of 4 N sodium hydroxide solution, mixed with a solution of 40 g. of magnesium chloride in 300 cc. of water, the whole cooled to −5° and then stirred mechanically. Ninety-five g. of sodium hydrosulfite is now gradually added in the course of two hours, care being taken that the temperature does not rise above 0°. After all of the hydrosulfite has been introduced, the mixture is stirred for another half hour, when the crude bromo-amino compound precipitates. This is filtered off, washed with a small volume of ice water and purified by dissolving in the least amount of 5% hydrochloric acid, rapidly filtering and neutralizing the cooled filtrate with dilute sodium hydroxide solution until faintly acid to Congo Red. After standing for a short time, the product crystallizes out from solution; it is filtered off, washed with water until free of chlorides and sulfates and then recrystallized from hot water to which Nuchar "W" has been added to decolorize; yield, 14 g. It forms colorless prisms which are soluble in hot water, almost insoluble in cold, insoluble in dilute alkali, dilute hydrochloric acid, ethyl and methyl alcohols, insoluble in acetone, ether and most organic solvents.

Anal. Calcd. for $C_6H_7O_4NAsBr$: N, 4.48; As, 24.04; Br, 25.64. Found: N, 4.35; As, 23.67; Br, 25.30.

5-Bromo-3-acetylamino-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2BrOH(NHOCCH_3)$.—This acid was prepared from the preceding amino compound (10.4 g.) by suspending it in water (100 cc.) and chopped ice (200 g.) and acetylating with acetic anhydride (6.9 g.) at reduced temperature. The whole is mechanically stirred for one hour and the resulting precipitate filtered off and purified by dissolving in *N* sodium hydroxide, decolorizing with Nuchar "W," filtering, cooling the filtrate and acidifying slightly with hydrochloric acid, using Congo Red as an indicator; yield, 6 g. It gives colorless prisms which are soluble in water, 10% hydrochloric acid, dilute alkalies, ethyl and methyl alcohols, but insoluble in ether. It darkens at 267–270° but remains unmelted at 300°.

Anal. Calcd. for $C_8H_9O_5NAsBr$: N, 3.95; As, 21.18. Found: N, 3.88; As, 21.19.

N-Acyl Derivatives of 3,5-Diamino-4-hydroxyphenylarsonic Acid

3,5-Diamino-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2(OH)(NH_2)_2 \cdot {}^1/_2H_2O$.—This compound was first described in a German patent.[6] The method of preparation was later modified by Raiziss and Gavron[5] and still further improved by Raiziss and Fisher.[7] It is obtained by reducing 3,5-dinitro-4-hydroxyphenylarsonic acid with sodium hydrosulfite at low temperature, and is purified by dissolving in dilute hydrochloric acid, filtering and neutralizing the filtrate with dilute sodium hydroxide.

Anal. Calcd. for $C_6H_9O_4N_2As \cdot {}^1/_2H_2O$: N, 10.89; As, 29.18; H_2O, 3.50. Found: N, 10.76; As, 29.00; H_2O, 3.10.

3,5-Di-(formylamino)-4-hydroxyphenylarsonic Acid, $H_2O_3As \cdot C_6H_2(OH)(NHOCH)_2$.—A mixture of 10 g. of 3,5-diamino-4-hydroxyphenylarsonic acid and 30 cc. of 85% formic acid is allowed to react at room temperature overnight, then diluted with 300 cc. of water and cooled. The crude diformyl derivative, which precipitates out, is filtered off, washed with water until free from acid, and finally recrystallized from hot water, using Nuchar as a decolorizing agent; yield of recrystallized product, 5 g.

It forms colorless, short, spear-shaped needles which are very sparingly soluble in cold water, soluble in dilute aqueous sodium hydroxide, ethyl or methyl alcohol, in-

---

[6] German Patent 224,953 (1910).

[7] Raiziss and Fisher, to be published in "Organic Syntheses."

soluble in most other organic solvents, and is decomposed by hydrochloric acid. When heated it starts to decompose rapidly at about 200° but remains unmelted at 275°.

Anal. Calcd. for $C_8H_9O_6N_2As$: N, 9.21; As, 24.67. Found: N, 9.21; As, 24.52.

The sodium salt of this compound was prepared by dissolving it in aqueous sodium hydroxide and precipitating with 10 volumes of ethyl alcohol.

3,5-Di-(acetylamino)-4-hydroxyphenylarsonic acid, $H_2O_3AsC_6H_2(OH)(NHOCCH_3)_2$, prepared according to the method of Raiziss and Gavron[5] and recrystallized from water, using Nuchar as a decolorizer, is obtained in clusters of colorless needles. It is soluble in boiling water, but only sparingly so in cold, soluble in cold dilute aqueous alkalies, insoluble in dilute acids and the usual organic solvents. It darkens at 235–240° but does not melt at 275°.

Anal. Calcd. for $C_{10}H_{13}O_6As$: N, 8.43; As, 22.60. Found: N, 8.09; As, 22.48.

3,5-Di-(propionylamino)-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2(OH)(NHOCCH_2CH_3)_2$.—12.4 g. of 3,5-diamino-4-hydroxyphenylarsonic acid is suspended in 50 cc. of water, 14.3 g. of propionic anhydride added and the whole refluxed for ten minutes. After diluting with 50 cc. of water and cooling, 10 cc. of concentrated hydrochloric acid is added. The resulting precipitate is filtered off, washed several times with 10% hydrochloric acid, then with water until free of chlorine ions and recrystallized from water, using Nuchar to decolorize; yield, 6 g.

The dipropionyl compound crystallizes in long, colorless silky needles, soluble in hot water, sparingly so in cold water, soluble in dilute aqueous alkalies, insoluble in dilute acids or the usual organic solvents except methyl alcohol, in which it is sparingly soluble. When heated it melts at 197–198° to a dark red liquid.

Anal. Calcd. for $C_{12}H_{17}O_6N_2As$: N, 7.78; As, 20.83. Found: N, 7.77; As, 20.53.

3,5-Di-(butyrylamino)-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2(OH)(NHOCCH_2CH_2CH_3)_2$, is prepared from butyric anhydride like the corresponding propionyl compound, except (1) that 5 g. of copper turnings must be added as a catalyst and (2) after cooling the reaction mixture it is not necessary to dilute with water before precipitating with concentrated hydrochloric acid. It crystallizes from hot water in colorless needles, m. p. 177°, soluble in acetone and methyl alcohol; with other solvents it behaves like the preceding compound.

Anal. Calcd. for $C_{14}H_{21}O_6N_2As$: N, 7.21; As, 19.33. Found: N, 7.08; As, 19.57

3,5-Di-(chloro-acetylamino)-4-hydroxyphenylarsonic Acid, $H_2O_3AsC_6H_2(OH)(NHOCCH_2Cl)_2$.—To a solution of 24.8 g. of 3,5-diamino-4-hydroxyphenylarsonic acid in 200 cc. of *N* sodium hydroxide solution, 22.6 g. of chloro-acetyl chloride is slowly added during fifteen minutes while stirring rapidly. The reaction starts immediately with considerable evolution of heat. The mixture is then cooled, stirred for one-half hour longer and the desired product obtained by the addition of 20 cc. of concentrated hydrochloric acid. It is filtered off, suspended in 10% hydrochloric acid, again filtered and washed, first with 10% hydrochloric acid, then with water until free of chlorine ions. It is finally purified by recrystallizing from 10% acetic acid, using Nuchar to decolorize.

The compound separates as colorless needles, darkening at 200° and melting with decomposition at 210–211°. It is soluble in dilute aqueous alkalies, methyl alcohol and boiling dilute acetic acid, very sparingly so in hot water, practically insoluble in cold water and insoluble in acetone or ether.

Anal. Calcd. for $C_{10}H_{11}O_6N_2AsCl_2$: N, 6.98; As, 18.70. Found: N, 6.77; As, 19.17.

The sodium salts of these 5 acyl derivatives were prepared but not analyzed.

Summary

1. The following compounds have been prepared and described for the first time: (a) The lithium, calcium, barium and strontium salts of 3-acetylamino-4-hydroxyphenylarsonic acid; (b) 5-bromo-3-nitro-4-hydroxyphenylarsonic acid, 5-bromo-3-amino-4-hydroxyphenylarsonic acid and 5-bromo-3-acetylamino-4-hydroxyphenylarsonic acid; (c) 3,5-di-(formylamino)-, 3,5-di-(propionylamino)-, 3,5-di-(butyrylamino)-, 3,5-di-(chloro-acetylamino)-4-hydroxyphenylarsonic acids and their sodium salts.

2. 5-Bromo-3-amino-4-hydroxyphenylarsonic acid is neither more trypanocidal or spirocheticidal than 3-amino-4-hydroxyphenylarsonic acid or its N-acetyl derivative.

3. The least toxic of all the compounds discussed in this paper is 3,5-di-(acetylamino)-4-hydroxyphenylarsonic acid. When injected intravenously into white rats its maximum tolerated dose is 4.6 times greater than that of 3-acetylamino-4-hydroxyphenylarsonic acid.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 593]

THE SYNTHESIS OF 6-HYDROXYPIPERONYLIC ACID AND INCIDENTAL COMPOUNDS

BY MARSTON TAYLOR BOGERT AND FRANK ROSE ELDER[1]

RECEIVED OCTOBER 1, 1928 PUBLISHED FEBRUARY 5, 1929

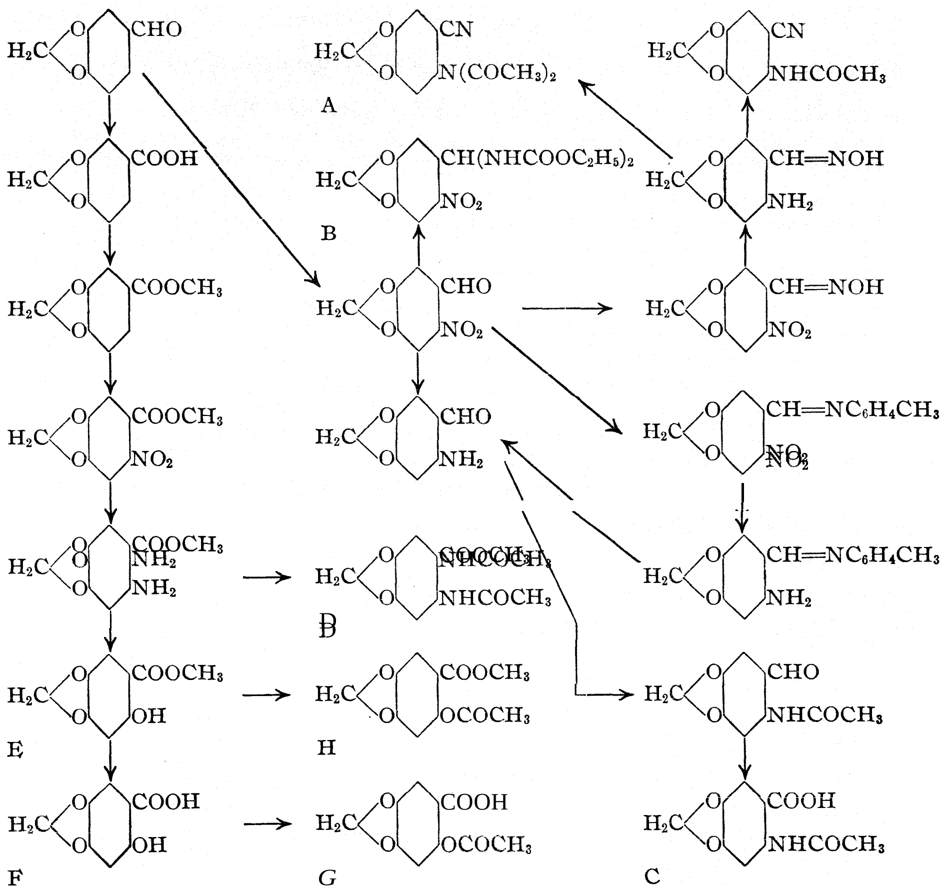
Salicylic acid and its derivatives, notably acetyl-salicylic acid (Aspirin), have proved to be of sufficient therapeutic value to justify additional experimental work for the purpose of gaining more light upon the connection between chemical constitution and physiological effect in the group of the o-hydroxybenzoic acids.

The experimental work which follows describes the synthesis of 6-hydroxypiperonylic acid, some of its derivatives and incidental products. This particular acid was selected because we failed to find any description of it in the literature, because it is structurally the methylene ether of a dihydroxysalicylic acid and because of the fact that the methylene-dioxy grouping is of frequent occurrence in natural products, including certain of the alkaloids.

The various lines of approach to this goal are sufficiently indicated in the flow diagram. The route via piperonylic acid proved most satisfactory, for reasons set forth in the Experimental Part.

---

[1] Based upon the Dissertation submitted by Dr. Elder in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University, 1927. An abstract of this paper was read before the Division of the Chemistry of Medicinal Products, at the Richmond Meeting of the American Chemical Society, April, 1927.



It is worth noting that methyl 6-hydroxypiperonylate, in contradistinction to methyl salicylate, possessed only an exceedingly faint agreeable odor, without any of the wintergreen character. Similarly, the methyl ester of the 6-aminopiperonylic acid was a colorless and practically odorless crystalline solid, with none of the aroma peculiar to methyl anthranilate.

Of the 6-hydroxypiperonylic acid, and of its acetyl derivative, sufficient material has not been accumulated as yet to proceed with the pharmacological tests.

Heretofore, 6-aminopiperonal has been obtained only indirectly from the 6-nitro compound, through the reduction of the *p*-toluidine derivative of the latter and hydrolysis of the resultant 6-aminopiperonylidene-*p*-toluidine, all attempts at the direct reduction of the nitro-aldehyde itself having failed. We have found that this direct reduction of the nitro to the amino-aldehyde can be accomplished with ferrous sulfate and ammonia, under proper conditions, with a yield of 60%.

Experimental

6-Nitropiperonal was prepared by the process of Salway,[2] with certain modifications which were found to give larger yields, as follows.

To 500 cc. of concentrated nitric acid (sp. gr. 1.42) cooled to 0°, there was added 50 g. of finely pulverized piperonal slowly and with constant stirring, the temperature being maintained below 0° during this addition and for two to three hours thereafter. If some of the piperonal still remained undissolved, the freezing mixture was removed and the mixture allowed to warm gradually, until all was dissolved. The solution was poured immediately into ice water, the yellow precipitate collected, washed free from nitric acid and stirred with sufficient 40% sodium bisulfite solution to make a thick paste. Two volumes of water were added and the mixture filtered. The residue was subjected to the same treatment and this was repeated with the two or three succeeding residues. The combined filtrates were made alkaline with sodium hydroxide, the precipitate collected, washed thoroughly and crystallized from a 1:1 mixture of ethyl acetate and alcohol. The nitropiperonal so obtained formed long, pale yellow needles, m. p. 97–98' (corr.) (Salway gives 98°); yield, 46 g., or 70%. There was recovered also 14 g. of 4-nitro-1,2-methylenedioxybenzene which, taken together with the nitropiperonal, accounts for 96% of the piperonal used. The formation of this by-product, through replacement of the aldehyde group during the nitration, was noted first by Salway.

6-Nitropiperonylidene-diurethan.—In 1913 Bianchi[3] condensed piperonal with ethylurethan and obtained a product in good yield which was easily hydrolyzed. Experiments were conducted therefore with nitropiperonal, for the purpose of preparing a similar urethan condensation, to be reduced to the corresponding amino derivative and the latter hydrolyzed to the 6-aminopiperonal.

A mixture of 5 g. of nitropiperonal and 4.86 g. of ethylurethan was heated at 100–110°. To the clear yellow melt there was added 1 cc. of concentrated hydrochloric acid, the mixture was well stirred and the heating continued until the evolution of vapor ceased. The hydrochloric acid addition caused the mixture to turn first green, then brown and finally black, and nearly solid. It was left overnight, then dissolved in a mixture of alcohol, chloroform and acetone, boiled for several hours with a decolorizing carbon, filtered and the filtrate concentrated. The brownish product which separated was collected, washed with a little cold alcohol, boiled in ethyl acetate solution with a decolorizing carbon and the filtrate concentrated and cooled. There separated a fine, feathery solid, with a faint yellowish-green tinge, which melted with decomposition at 207–208" (corr.); yield, 1 g., or 10%. On long exposure to the light, its color changed to a yellowish brown. For analysis, the product was dried to constant weight at 110–115°.

Anal. Calcd. for $C_{14}H_{17}O_8N_3$: C, 47.32; H, 4.83; N, 11.83. Found: C, 47.10, 46.67; H, 5.27, 4.94; N, 11.98.

Considerable difficulty was experienced in purifying this product through failure to find any satisfactory solvent or mixture of solvents. It dissolved in both acids and alkalies, and when dry was exceedingly light, fluffy and triboelectric. Because of these unpromising results, further work along this line was abandoned.

6-Nitropiperonal **Oxime.**—Haber[4] described this oxime but gave no

---

[2] Salway, J. *Chem. Soc.*, **95,** 1155 (1909).

[3] Bianchi, *Gazz. chim. ital.*, *43,* I, 237 (1913).

[4] Haber, **Ber.,** 24, 625 (1891).

details concerning its preparation or yield. We found that dry potassium carbonate as a condensing agent gave better results than zinc oxide.

To an alcoholic solution of the aldehyde (10 g.) and hydroxylamine hydrochloride (*3.6* g.), there was added dry potassium carbonate (3.6 g.) dissolved in a little water, and the mixture was boiled for three hours. The yellow oxime which separated as the mixture cooled, when recrystallized from alcohol, melted at 201–203° (corr.); yield, 84% (9 g.). Haber gave the m. p. as 203°.

6-Aminopiperonal oxime was prepared from the nitro oxime by reduction in alcoholic solution with ammonia and hydrogen sulfide, essentially as described by Haber.[4] Decolorized and crystallized from alcohol, it formed nearly colorless, glistening needles. m. p. 182–183° (corr.); yield, 81%. Haber recorded the melting point as 175.5°.

6-Acetaminopiperonylonitrile.—Haber[4] reported that when he heated the above amino oxime for a short time with excess of acetic anhydride and sodium acetate, the acetaminopiperonylonitrile, m. p. 216° (corr.) resulted. We found that, depending upon the duration of this heating, the product was either the mono- or the diacetyl derivative.

A mixture of 2 g. of the amino oxime, 1 g. of fused sodium acetate and 20 g. of acetic anhydride was boiled for ten to twelve minutes and then poured into an excess of cold dilute sodium carbonate solution. The precipitate (1 g.) was collected, washed, crystallized from alcohol and then from chloroform. A small amount (0.3 g.) of fine, feathery needles was thus secured, m. p. 215–217° (corr.), which was dried *in vacuo* over concentrated sulfuric acid and analyzed.

And. Calcd. for $C_{10}H_8O_3N_2$: C, 58.82; H, 3.92; N, 13.73. Found: C. 58.78; H, 4.22; N, 13.82.

Briefer heating gave no appreciable quantity of this mono-acetyl derivative. In boiling ethyl or iso-amyl acetate solution, the acetylation failed wholly, and the amino oxime was recovered unaltered.

The yield of mono-acetyl derivative noted did not seem to us sufficient to make this route of approach to our goal a very promising one and the work was discontinued.

6-Diacetaminopiperonylonitrile.—When the amino oxime (2.5 g.), fused sodium acetate (2 g.) and acetic anhydride (15 g.) were boiled together for an hour, the mixture poured into the dilute carbonate solution and the precipitate crystallized from alcohol, thin plates (1.5 g.) were obtained, m. p. 115–122° (corr.). These were dissolved in chloroform (10 cc.) cold. Spontaneous evaporation of the solvent yielded colorless, thin rectangular plates, m. p. 146–147' (corr.), which were dried *in vacuo* over concentrated sulfuric acid and analyzed.

And. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.54; H, 4.07; N, 11.38. Found: C, 58.64; H, 4.18; N, 11.92, 11.93.

6-Nitropiperonylidene-*p*-toluidine.—Rilliet and Kreitmann,[5] after reviewing the failure of other workers to obtain 6-aminopiperonal by direct reduction of the nitro-aldehyde, succeeded in preparing it indirectly through the *p*-toluidine derivative of the latter.

On repeating this work, we found that the use of a 20% excess of *p*-toluidine gave a much better yield of the condensation product (90% instead of 75%). Since this product is very sensitive to the light, rapidly turning dark red, the condensation and subsequent crystallization were carried out in the dark, and long glistening yellow needles

---

[5] Rilliet and Kreitmann, *Compt. rend.*, 157,782 (1913).

were thus secured, m. p. 121–122° (corr.). Rilliet and Kreitmann gave the m. p. as 121.5°.

6-Aminopiperonylidene-*p*-toluidine was prepared from the nitro derivative by reduction in alcoholic solution with sodium sulfide, as described by Rilliet and Kreitmann.[5] The crude product (yield, 60%) was crystallized twice from alcohol and then once from benzene. Small rosets of fine, silky yellow needles resulted, m. p. 137–138° (corr.); yield, 12%. Rilliet and Kreitmann reported a yield of 54% and a melting point of 134.5°. Our product was dried *in vacuo* over concentrated sulfuric acid and analyzed.

Anal. Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.82; H, 5.60; N, 11.02. Found: C, 70.61; H, 5.85; N, 10.89.

We tried also the reduction method of Cobenzl,[6] using sulfur and sodium sulfide in alcoholic solution, but the yield of amino derivative was less.

6-Aminopiperonal.—Rilliet and Kreitmann[5] stated that they hydrolyzed the p-toluidine derivative by boiling it with dilute sodium hydroxide. Judging by our own experience, they must have meant an alcoholic and not an aqueous alkaline solution, for we found that twenty hours' boiling with a 10% aqueous sodium hydroxide solution was without effect. However, it was easily hydrolyzed as follows.

A solution of 6 g. of the p-toluidine derivative and 15 g. of potassium hydroxide in 300 cc. of alcohol was boiled under a reflux condenser for three to four hours, an equal volume of water added and steam blown through as long as any p-toluidine came over. The residual liquid was filtered hot and as the filtrate cooled yellowish needles of the aminopiperonal separated which were crystallized from water and then melted at 107–108° (corr.); yield, about 50%. Rilliet and Kreitmann gave the m. p. as 107°.

The direct reduction of 6-nitropiperonal has been essayed unsuccessfully by various investigators,[7] and we were equally unsuccessful when we attempted to apply the method used by Bamberger and Demuth[8] for the reduction of o-nitrobenzaldehyde to the amino-aldehyde, by the use of titanous chloride,[9] or by the action of hydrogen sulfide and ammonia. We were more fortunate, however, when we tried ferrous sulfate and ammonia.[10]

To a solution of 100 g. of ferrous sulfate in 500 cc. of boiling water there was added a hot aqueous solution of 10 g. of nitropiperonal, followed by about 100 cc. of concentrated ammonium hydroxide solution in small portions, until the solution was alkaline to litmus. After boiling the mixture for five minutes, it was filtered, the precipitate washed thoroughly with boiling water and the filtrate and washings were combined and cooled. The crude amino-aldehyde which separated was recrystallized from water and then formed long yellow needles, m. p. 107–108° (corr.), identical with that obtained by the Rilliet and Kreitmann method; yield, 5 g., or 60%.

Attempts to replace the amino group by hydroxyl, through the diazo reaction, proved futile.

---

[6] Cobenzl, *Chem.-Ztg.*, 39, 859 (1915).

[7] (a) Haber, *Ber.*, 24, 625 (1891); (b) Friedländer and Schreiber, *ibid.*, 28, 1385 (1895); (c) Oertley, "Thése," Université de Genève, 1910.

[8] Bamberger and Demuth, *ibid.*, 34, 1330 (1901).

[9] (a) Knecht, *ibid.*, 36, 166 (1903); (b) Sachs and Sichel, *ibid.*, 37, 1862 (1904).

[10] Jacobs and Heidelberger, THIS JOURNAL, 39, 1435 (1917).

Acetyl Derivative.—Colorless needles (from water), m. p. 161–162° (corr.). Rilliet and Kreitmann gave the melting point as 160°.

6-Acetaminopiperonylic Acid.—The 6-acetaminopiperonal (3 g.) was oxidized by potassium permanganate in the presence of magnesium sulfate, and the crude product crystallized from dilute alcohol in faintly yellowish, long feathery needles, m. p. 124–125° (corr), soluble in alcohol but difficultly soluble in water; yield, 0.4 g. It was dried in *vacuo* over concentrated sulfuric acid and analyzed.

And. Calcd. for $C_{10}H_9O_5N$: C, 53.81; H, 4.03. Found: C, 52.97, 54.13; H, 4.09, 4.81.

While these analytical results are not very satisfactory, they are sufficiently close, if considered in conjunction with the method of preparation, to support the assumption that the product was the acid stated. No material was left for further analyses and the preparation was not repeated.

Piperonylic acid was prepared most conveniently as follows. To 3 liters of water, there was added 50 g. of finely powdered piperonal and the mixture was heated to 40–50°, stirred mechanically and potassium permanganate solution run in slowly until the odor of piperonal was no longer perceptible. This required generally about 125 g. of the permanganate. Excess of the latter, if any, was destroyed by the addition of a little alcohol, the mixture filtered hot and the filtrate acidified with hydrochloric acid. The piperonylic acid which separated as the solution cooled was practically pure; yield, 36 g., or 65%.

When the oxidation was conducted in acetone, instead of in aqueous solution, the yield was about the same. Oxidation in the presence of magnesium sulfate, however, resulted in considerably lower yields.

Methyl 6-Aminopiperonylate.—Piperonylic acid was converted into its methyl ester, the latter nitrated and the nitro ester reduced to the 6-amino ester, as described by Oertley and Pictet[11] and with similar results.

Acetyl Derivative.—Colorless, fine fluffy needles (from alcohol), m. p. 183–184" (corr.); soluble in alcohol, acetone, chloroform or benzene, less so in ether, and but slightly soluble in water. It was dried *in vacuo* over concentrated sulfuric acid and analyzed.

Anal. Calcd. for $C_{11}H_{11}O_5N$: C, 55.70; H, 4.64. Found: C, 55.63, 55.88; H, 4.83, 4.93.

Methyl 6-Hydroxypiperonylate.—The conversion of the amino into the hydroxy ester proved to be a rather troublesome task. When the diazotized ester was boiled with water, subjected to a current of steam, or dropped into a boiling borax solution, a dark red product resulted from which we were unable to recover any of the desired hydroxy ester. The problem was finally solved as follows.

To a well-cooled solution of 5 g. of the amino ester in 10 g. of concentrated sulfuric acid and 25 cc. of water, there was added 2.15 g. of potassium nitrate in 10 cc. of water and the diazo solution was dropped slowly into a boiling solution of 25 g. of copper sulfate in 25 cc. of water. The resultant solution was poured into 400–500 cc. of water and the mixture left overnight at room temperature. The reddish-brown precipitate was collected, washed thoroughly with water, decolorized in boiling alcoholic solution and the filtrate allowed to cool, There separated colorless rosets, m. p. 97–98° (corr.); yield, 50%. This proved to be a mixture of the desired ester with a small amount of 6-hydroxypiperonylic acid. It was therefore shaken first with a dilute sodium car-

---

[11] Oertley and Pictet, Ber., 43, 1336 (1910).

bonate solution, to remove the free hydroxy acid, and the residue then extracted with dilute sodium hydroxide solution. The use of too strong a caustic alkali solution must be avoided. The caustic soda extracts were acidified, the colorless precipitate was collected, washed, dried, dissolved in a mixture of alcohol and ether and the solvent allowed to evaporate spontaneously. The hydroxy ester crystallized in small colorless rosets, m. p. 99–100° (corr.), which were practically odorless and gave a deep blue color with ferric chloride solution. These crystals were dried *in vacuo* over concentrated sulfuric acid and analyzed.

Anal. Calcd. for $C_9H_8O_5$: C, **55.10;** H, **4.11.** Found: C, **55.19;** H, **4.28.**

The acetyl derivative, from the ester and acetyl chloride, was decolorized in ether solution and then separated in nearly colorless crystals, m. p. 50–60°. Recrystallized from a mixture of alcohol and ether, it formed rosets of nearly colorless needles, m. p. **97–98'** (corr.); yield, **3.5** g. or 60%. For analysis, it was dried *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $C_{11}H_{11}O_6$: C, **55.46;** H, **4.20.** Found: **C, 55.29;** H, **4.25.**

6-Hydroxypiperonylic Acid.—The methyl ester was hydrolyzed by boiling it for about an hour in dilute (5%) potassium hydroxide solution until a test portion no longer yielded a precipitate when saturated with carbon dioxide. The slightly reddish solution was acidified with dilute hydrochloric acid, the precipitate collected, washed and dried; yield, 7 g. or 80%. Recrystallized from either chloroform or dilute alcohol, it formed nearly colorless fluffy needles, m. p. **211–212"** (corr.), easily soluble in alcohol, but only slightly in water, ether, chloroform or benzene. For analysis it was dried *in vacuo* over concentrated sulfuric acid; (a) was crystallized from alcohol, and (b) from chloroform.

Anal. Calcd. for $C_8H_6O_5$: C, **52.74;** H, **3.29.** Found: **C,** (a) **52.38,** (b) **52.45;** H, (a) **3.24,** (b) **3.26.**

With ferric chloride solution, this acid gave the same deep blue color as its methyl ester.

6-Acetoxypiperonylic Acid.—Very great difficulty was experienced in the preparation of this aspirin by direct acetylation of the hydroxy acid and no satisfactory method was worked out, although a great deal of experimental work was done and many different processes were tried.

About equal parts of the hydroxy acid and fused sodium acetate were dissolved in acetic anhydride, an excess of acetyl chloride was added, the mixture boiled for six to eight hours, cooled, poured into a large volume of cold water and the precipitate removed, washed and dried. Fractional crystallization of this product from acetic anhydride, repeated **5** or **6** times, washing the crystals each time with a little cold ether, finally yielded a small quantity of nearly colorless needles, which melted at 155.5–156.5° (corr.), with slight preliminary softening, were freely soluble in alcohol, glacial acetic acid or acetic anhydride and dissolved but slightly in water, ether, chloroform or benzene.

Anal. Calcd. for $C_{10}H_8O_6$: C, **53.57;** H, **3.57.** Found: C, **53.77;** H, **3.96.**

Summary

1. 6-Hydroxypiperonylic acid and its acetyl derivative, the former a derivative of salicylic acid and the latter of aspirin have been synthesized from piperonal, for the purpose of pharmacological investigation.

2. It has been shown that 6-nitropiperonal can be reduced directly to the amino aldehyde by the use of ferrous sulfate and ammonia.

3. Other derivatives of piperonal and of piperonylic acid have been prepared and described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF THE HEMOCYANIN OF LIMULUS POLYPHEMUS

BY THE SVEDBERG AND FRANCIS F. HEYROTH[1]

RECEIVED OCTOBER 2, 1928 PUBLISHED FEBRUARY 5, 1929

Gross differences have been reported by several workers[2] in the copper content, oxygen-combining curves, isoelectric points and various other properties of the hemocyanins obtained from different animals. This investigation was undertaken to determine whether a similar difference could be observed in the molecular weights of the hemocyanins or respiratory pigments of two species, the vineyard snail, Helix *pomatia*, and the horseshoe crab, Limulus polyphemus. Measurements in the ultracentrifuge by Svedberg and Chirnoaga have shown the former protein to have a molecular weight of 5,000,000 in solutions containing 0.05–0.1% of hemocyanin near the isoelectric point, 5.2. The copper contents of the hemocyanins of *Limulus* and Helix are 0.17 and 0.28%, respectively.[3]

Experimental

Preparation of Material.—We are indebted to Dr. A. C. Redfield for a sample of the hemocyanin of Limulus prepared by him at Woods Hole in 1926. He has described its preparation as follows:[3] "The fresh serum from a large number of animals was salted out by the addition of ammonium sulfate to half saturation, and in this condition preserved for some six months. The precipitated hemocyanin was separated by filtration, redissolved in 5% saturated ammonium sulfate containing 0.001 N ammonium hydroxide, filtered free of all insoluble residue, and reprecipitated by adding just sufficient saturated ammonium sulfate. This precipitate was separated by centrifugation. In order to secure a satisfactory separation, it was found desirable to bring the reaction to approximately PH 8.0 by the addition of ammonium hydroxide. The process of redissolving and salting out was then repeated two more times."

The material so prepared was dissolved in 5% saturated ammonium sulfate and further purified by dialysis before beginning this series of experiments. The dialysis was conducted in collodion bags in the ice chest against *N*/10,000 and later *N*/1000

---

[1] Fellow in Medicine of the National Research Council.

[2] References in Svedberg and Chirnoaga, THIS JOURNAL, 50, 1399 (1928), and in the papers of Stedman and Stedman, *Biochem.* J., 20, 938, 949 (1928).

[3] Redfield, Coolidge and Shotts, *J. Biol. Chem.*, *76*, 185 (1928).

sodium hydroxide. After three weeks the alkali was replaced by distilled water, which was repeatedly changed during a month.

The suspension obtained had a specific electrical conductivity of 1.07×10^{-5} mho. The solubility of the hemocyanin of *Limulus* in electrolyte solutions is not as great as that of *Helix,* a suspension of which may be brought into solution by the addition of but traces of salts. A 2.27% stock solution of the *Limulus* hemocyanin was made from the supension by adding **3** cc. of $M/15$ $Na_2HPO_4 \cdot 2H_2O$ and *1.5* cc. of $M/15$ KH_2PO_4 per *100* cc. of final solution. The reaction of this solution, PH *6.63* (electrometrically determined), permitted the preparation of a sufficiently concentrated solution for the pycnometric determination of the partial specific volume, V, of the protein. At the same time the reaction was judged to be not too **far** from the isoelectric point of the protein. This is not accurately known, Stedman and Stedman[2] merely stating that the method of maximal precipitation indicates it to be somewhat greater than *6.3.* Toluene was employed as a preservative as it is readily removed from the solutions just before use by bubbling nitrogen gas through them.

The partial specific volume was determined by the pycnometric method described for the other proteins studied in this Laboratory. The concentration of the solutions was determined by transferring *1* cc. of the solution to a porcelain crucible, evaporating down to coagulation on a water-bath and then drying to constant weight at 105°. The content of anhydrous salt per cc. of the solution was subtracted from this weight. The mean value of V obtained in three determinations at two protein concentrations was *0.735* at 20°. This is, within the limits of experimental error, the same as that of the hemocyanin of *Helix.*

Preliminary measurements of the visible and ultraviolet light absorption showed the hemocyanin of *Limulus* to possess in general the same type of absorption curve as that obtained from *Helix.* In the experiments here reported the light absorption in the short-waved ultraviolet region only was employed. Chlorine and bromine filters were used as previously described[4] for the isolation of this region of the radiations from a quartz mercury vapor lamp.

Determination of the Molecular Weight

A. Sedimentation Velocity Method.—In this method the molecular weight is given by the equation $M = RTs/D(1 - V\rho)$ in which s is the specific sedimentation velocity or rate of movement of the protein under unit centrifugal field expressed in cm. per second, D is the diffusion constant expressed in cm.^{2} per day, ρ the density of the solution, R the gas constant and T the absolute temperature. The ultracentrifuge designed for low and medium centrifugal fields was employed in all of the runs. A speed of approximately *8400* r.p.m. *(4100* times the force of gravity) was used and each run was continued for seven and a half hours, as this hemocyanin did not move down as rapidly as did that of *Helix.* Since an increase in the concentration of *Helix* hemocyanin solutions has been shown to produce a great depression of the values of the diffusion constant, while affecting but slightly the specific sedimentation velocity, a series of runs with *Limulus* hemocyanin at concentrations varying from 0.03 to 0.98% was deemed necessary. Three different quartz cells were used to secure the necessary thickness of layer of the variously concentrated

---

[4] Svedberg and Nichols, **THIS** JOURNAL, 48, *3081 (1926).*

solutions necessary in order to secure photographs of suitable contrast by means of exposures of from fifteen to forty-five seconds. Thus, the thickness of the layer of solution used was 2 mm. for 0.65 and 0.98% solutions, 8 mm. for the range of 0.09 to 0.12%, and 14 mm. for the more dilute solutions of 0.03 to 0.06%. Imperial process plates were employed. Dilutions of the stock solution into phosphate buffer of PH 6.63 were made immediately before each run. The results of each of the runs are given in Table I, in which Col. 1 gives the concentration of the protein, Col. 2 the specific sedimentation velocity and Col. 3 the diffusion constant. In almost all of the runs fifteen values of each were calculated at successive half-hour intervals. In the case of the diffusion constants the first three values in each series have been omitted and then only the next ten following values have been employed in the calculation of the mean value for each run. The first three values are inaccurate as, since the rate of centrifugation was not great under the centrifugal field employed, no region of pure buffer had yet appeared. The last few values are also in most cases in error because there is then no longer present a region of the solution within which there is no change of concentration with distance from the center of rotation.

TABLE I

SEDIMENTATION VELOCITY MEASUREMENTS

Concn., *g.* per 100 cr.	*s*, cm./sec. × 10^{12}	*D*, cm.^{2}/day	"Concentration" of non-centrifugible matter
0.98	3.59	0.0139	3 "%"
.65	3.65	.0189	5.5
.13[a]	3.48	.0190	17.5
.12	3.32	.0178	8
.09	3.74	.0227	17
.OB	3.52	.0141	19
.06	3.55	.0162	18
.06	3.28	.0146	21
.03	3.74	.0221	103?
.03	3.79	.0181	49
Mean	3.57	.0177	
Mean using only the runs free from a drift in D.		.0147	

[a] This solution was made from the precipitate obtained by dialyzing a 0.03% solution. See section on Reversibility of the Disintegration.

The values of *s* are fairly constant throughout the range studied and show no definite trend with change of concentration. The diffusion values are, however, very irregular and lead to great variations in the molecular weights calculated in each of the runs. Thus the molecular weights vary from 1.31 × 10^6 to 2.05 × 10^6. Such variations point to the possibility that more than one variety of light-absorbing substance may be present in the solutions employed. That such is the case becomes apparent from a consideration of the drift with time which occurs in the successive diffusion constants obtained during the course of several of the runs. Table II gives the values of the diffusion constants obtained at successive half-hour intervals, and these are seen to increase throughout several, but not all, of the runs. As has been previously explained, this excessive blurring of the protein solution–solvent boundary may result from the gradual separation arising from the sedimentation at different rates of two or more proteins of not very greatly different frictional resistances.

TABLE II

"APPARENT DIFFUSION CONSTANTS" AT SUCCESSIVE THIRTY-MINUTE INTERVALS DURING EACH RUN

	0.98%	**0.65%**	**0.12%**	**0.13%**	**0.09%**
4	0.0118	0.0157	0.0161	0.0143	0.0166
5	.0129	.0177	.0140	.0190	.0199
6	.0144	.0178	.0166	.0158	.0190
7	.0142	.0170	.0184	.0199	.0192
8	.0158	.0178	.0167	.0177	.0206
9	.0176	.0207	.0164	.0189	.0210
10	.0121	.0177	.0202	.0186	.0247
11	.0132	.0211	.0195	.0224	.0221
12	.0145	.0221	.0196	.0246	.0288
13	.0127	.0213	.0201	....	.0354
Mean	.0139	.0189	.0178	.0190	.0227

	0.06%	**0.06%**	**0.06%**	**0.03%**	**0.03%**
4	0.0096	0.0110	0.0107	0.0118	0.0161
5	.0098	.0136	.0115	.0132	.0160
6	.0107	.0154	.0120	.0158	.0206
7	.0169	.0184	.0136	.0265	.0207
8	.0148	.0184	.0161	.0184	.0161
9	.0167	.0180	.0193	.0266	.0286
10	.0139	.0162	.0156	.0134	.0254
11	.0139	.0175	.0161	.0199	.0258
12	.0152	.0168	....	.0196	.0249
13	.0192	.0165	.0168	.0155	.0271
Mean	.0141	.0162	.0146	.0181	.0221

The run at the concentration of 0.98% gave no indication of the presence of molecules of varying frictional resistance, but at 0.65 and 0.12% the presence of unlike molecules was clearly indicated. This effect was even more marked in solutions of 0.09%. When, however, the dilution was extended to 0.06%, it tended to disappear. In only one of three runs at this concentration could it be detected with certainty. The presence of such a condition in the two runs at 0.03% cannot be accurately determined as the contrast obtained with reasonable exposures was too small.

That the source of this non-uniformity of the protein molecules may well be a disintegration of the molecules present in the more concentrated solutions may be concluded from measurements of the light absorption in the region between the boundary of the protein and the meniscus of the solution. In the more concentrated solutions, 0.98 and 0.65%, these were never more than traces of light-absorbing material left in this region. The point on the concentration scale corresponding to the galvanometer reading given by the density in the photograph of this portion of the solution is in the following taken as a rough measure of the amount of non-centrifugible material present. The "concentrations" so stated do not give directly the actual concentration of the non-centrifugible material, since the value of $e/$ may conceivably (and in fact does) change as the units are disintegrated. Such "concentration" values have been given in Col. 4 of Table I and show clearly that the amount of non-centrifugible material increases from negligible amounts, 3–5% at 0.65% and over, to 17% upon dilution to 0.09%, and even to very high values in excess of 50% in 0.03% solutions. A possible interpretation of both the time drift in the diffusion constant and the formation of non-centrifugible material is as follows.

Dilution tends to cause a disintegration of the hemocyanin molecules. In the solutions which have been but slightly diluted only a comparatively small amount of non-centrifugible material is formed. This in itself is incapable of producing the drift with time in the diffusion values. At about 0.09 to 0.65% there is present, however, a certain amount of partly disintegrated or highly hydrated material which lowers but slightly the mean specific sedimentation velocity but which is capable of moving at such a rate in the centrifugal field as to produce the observed drift in the diffusion constants. In still more dilute solutions the disintegration process proceeds further, so that there are present fewer of the molecules in the first stage of disintegration (those which are responsible for the drift) and more of the more completely disintegrated and therefore non-centrifugible material. With increasing dilution as the decomposed material becomes more and more non-centrifugible, the drift in the diffusion values tends to disappear. The material which does centrifuge down in these dilute solutions may represent some of the original molecules which have escaped disintegration or may be possibly a more stable denaturation product of the same molecular weight as the protein present in the more concentrated solutions.

The progressive nature of the disintegration change due to dilution is indicated also by an effect noted in the latter part of some of the runs in dilute solutions and not noted in the case of other proteins. In the more dilute runs the successive curves tend to overlap each other in such a way as to indicate that during a given run non-centrifugible material is formed in increasing amounts. In each successive curve the light absorption increases in the region between the protein boundary and the meniscus. That a similar overlapping occurs also in the region in which the concentration is uniform indicates that the sum of the light absorption due to the presence of some large and some small molecules is greater than that due to the same amount of protein when present entirely as large, non-disintegrated molecules. The light absorption experiments reported in a later section point to the same possibility.

If the mean diffusionconstant, 0.0139, of only those runs (two at 0.06% and one at 0.98%) in which no marked drift with time in the values occurred is used, together with mean specific sedimentation velocity obtained from all of the experiments, a molecular weight of 1.90 X 10^6 is found. If only the diffusion constant obtained at 0.98% is used, the value is 2.04 × 10^6.

B. Sedimentation Equilibrium Method.—This method is based upon the attainment of an equilibrium in the cell between the centrifugation of the protein toward the bottom and its diffusion toward the top. A series of values for the molecular weight, M, is calculated by the equation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

for a series of portions ($x_2 - x_1$) of the column of liquid. R, T, p and ω have their usual meanings and c_1 and c_2 are the concentrations at the

TABLE III

SEDIMENTATION EQUILIBRIUM RUNS OF *Limulus* HEMOCYANIN

Part A

Concentration, 0.063%; Ph, 6.63; length of column of solution, 0.4 cm.; thickness of column, 1.4 cm.; distance of bottom of cell from the axis of rotation, 5.95 cm.; *T*, 293.2'; speed, 1929 r.p.m. ($\omega = 64.3\pi$). Exposures were 20, 40 and 60 seconds.

Distances, cm.		Mean concentration, %		
x_2	x_1	c_2	c_1	M
5.95	5.90	0.1503	0.1425	4.04 X 10^5
5.90	5.85	.1425	.1159	15.90 X 10^5
5.85	5.80	.1159	.0911	18.63 X 10^5
5.80	5.75	.0911	.0761	14.04 X 10^5
5.75	5.70	.0761	.0672	9.79 X 10^5
5.70	5.65	.0672	.0591	10.20 X 10^5
5.65	5.60	.0591	.0531	7.98 X 10^5

Part B

Concentration, 0.15%; Ph, 6.63; length of column of solution, 0.5 cm.; thickness of column, 0.8 cm.; distance of the bottom of the cell from the axis of rotation, 5.95 cm.; *T*, 293.2'; speed, 1929 r.p.m.; time exceeded 90 to 100 hours. Exposures were 50, 100 and 150 seconds.

x_2	x_1	c_2	c_1	M
5.95	5.90	0.1553	0.1496	2.84 X 10^5
5.90	5.85	.1496	.1413	4.38 X 10^5
5.85	5.80	.1413	.1290	7.05 X 10^5
5.80	5.75	.1290	.1189	6.36 X 10^5
5.75	5.70	.1189	.1086	7.13 X 10"
5.70	5.65	.1086	.0983	7.91 X 10^5
5.65	5.60	.0983	.0878	9.05 X 10^5
5.60	5.55	.0878	.0790	8.53 X 10^5
5.55	5.50	,0790	.0703	9.52 X 10^5

distances x_1 and x_2 from the axis of rotation. If the molecules of the protein solution have uniform frictional resistances, the successive values of M obtained at successive fractions of the way from the top to the bottom of the solution fluctuate irregularly about a mean value. The presence of a second type of molecule makes itself evident by a progressive increase in these values as the bottom of the cell is approached. The indication given by the sedimentation velocity method of the presence of more than one kind of molecule in 0.06–0.09% solutions was confirmed by the finding of a drift in the molecular weight values in an equilibrium run A of Table III. In this run equilibrium was attained in a column of solution, 0.06%, 4 mm. in height after eighty hours of centrifuging at a speed of 1900 r.p.m. The second run in Table III was made by using a 5-mm. column of a somewhat more concentrated 0.15% solution. In this case even after ninety to one hundred hours equilibrium had not been attained, as the concentration–distance curves at seventy-eight, ninety-one and one hundred hours did not coincide. It is probable that as the solution toward the central end of the cell becomes more dilute (0.07%) as equilibrium is approached, a disintegration of the molecules there occurs. Since this continues as the heavier molecules diffuse into this region, new conditions are set up, delaying greatly the attainment of a final state of equilibrium.

The Light Absorption of the Protein.—The light absorption of ***Limulus*** hemocyanin was measured in the visible region by means of a König-Martens spectrophotometer in a 2.86% solution at PH 6.74 and in the ultraviolet region by a modified Judd-Lewis spectrophotometer at a series of concentrations from **0.03** to 0.136%, corresponding to the range employed in the centrifuging experiments. In general the positions of the maxima of the absorption bands agree with those reported for ***Helix*** hemocyanin, although the values of ϵ/c are lower throughout than in the case of the latter protein. This is indicated in Fig. 1, which gives for comparison the light absorption curves of the two proteins. For the *Limulus* hemocyanin the values plotted in the ultraviolet were the mean of determinations at the concentrations 0.09 and 0.136%.

TABLE IV

LIGHT ABSORPTION OF THE HEMOCYANINS IN THE VISIBLE REGION

Wave *length,* μμ	*Limulus* 2.86%, **PH** 6.74	*Helix* 1.75%, **PH** 3.8	*Helix* 1.69%, **PH 5.6**	**Wave length,** μμ	*Limulus* 2.86%, **PH** 6.74	*Helix* **1.75%. PH** 3.8	*Helix* **1.69%, PH 6.6**
635	0.146	0.199	0.297	522	0.157	0.216	0.396
605	.158	.229	.339	506	.143	.206	.361
579	.178	.248	.377	492	.104	.200	.360
556	.176	.249	.395	479	.098	....	.349
538	.165	.238	.401	468	.093	.197	.346

The values of ϵ/c for the visible spectral region are given in Table IV and Fig. 2. It was shown by Svedberg and Chirnoaga that at *PH* **3.8** the maximum for *Helix* was shifted to the red and that the values over the whole region became relatively lower than those obtained at Ph **5.6.**

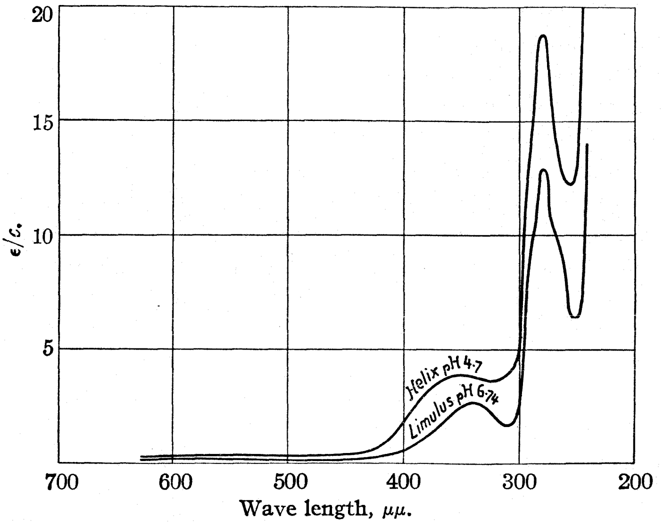


Fig. 1.

These changes accompanied a decomposition of the protein which has since been studied in detail. The values obtained for *Limulus* hemocyanin near its isoelectric point correspond more closely with those for the smaller particles of *Helix* which are present at *Ph* **3.8** than with the values for the larger molecules present at Ph **5.6.** The position of the maximum for *Limulus* hemocyanin also corresponds better with that of *Helix* at **3.8** than at **5.6.**

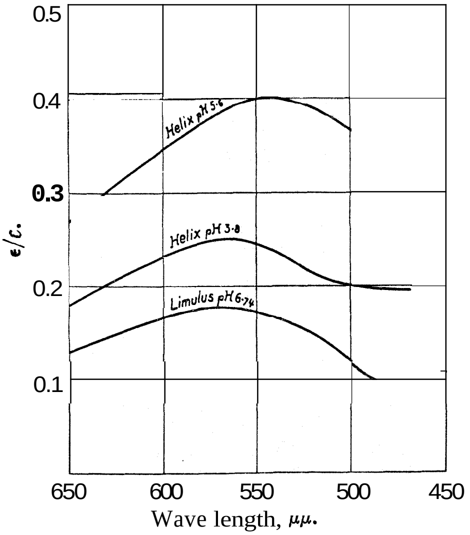


Fig. 2.

Although the accuracy of the measurements made with the Judd-Lewis apparatus in the ultraviolet is not as great as that of those in the visible made with the Konig-Martens spectrophotometer, two curves made at different concentrations of *Limulus* hemocyanin at *Ph* **6.63** are presented in Fig. **3,** as significant differences are shown which are readily reproducible. The measurements plotted indicate that Beer's law does not hold over this concentration range and that the light absorption increases as the concentration is lowered. This change in light absorption occurs in the same concentration range as that in which the sedimentation velocity and equilibrium runs had indicated the protein to undergo a change leading to the production of units of lesser magnitude. This change occurs over the entire ultraviolet region but is most evident on the broad maximum between 360–330μμ. This region is shown on a larger scale in Fig. 4, in which values at several concentrations are plotted. It appears here that the minimum which occurs at about 300–315μμ in the more concentrated solutions is by dilution shifted toward the longer wave lengths.

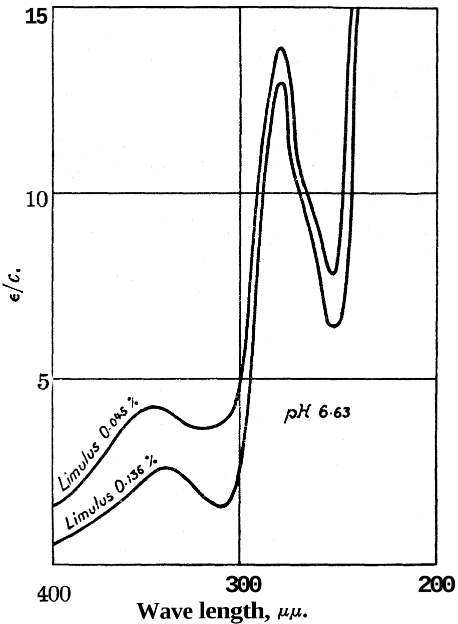
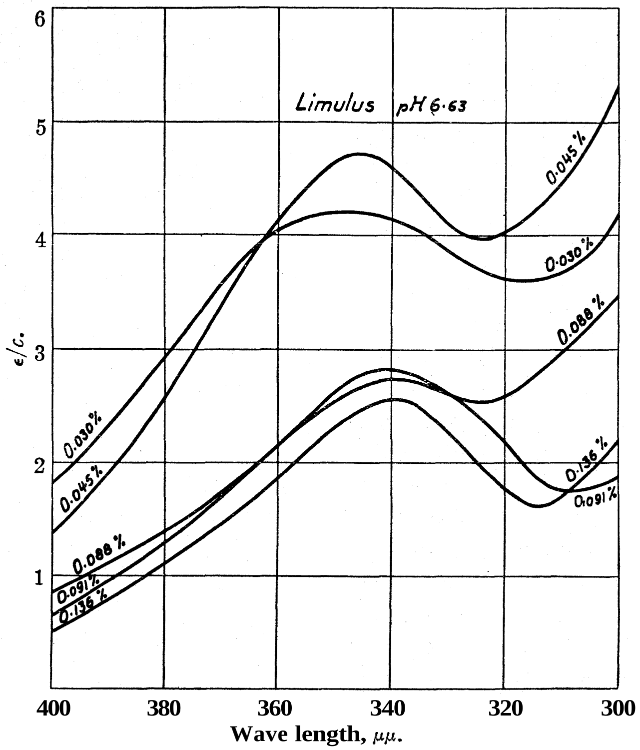


Fig. 3.

Reversibility of the Decomposition.—The light absorption of a portion of a 0.03% solution of *Limulus* hemocyanin was measured in a 20-mm. cell. After twenty-four hours the remainder of the solution was dialyzed against distilled water until a precipitate appeared. This was then dissolved to form an 0.088% solution at PH 6.63 and the light absorption was again measured. Fig. 4 shows that the light absorption of this solution corresponded to about that which had been previously obtained by using a solution of 0.09%. In a repetition of this experiment the reprecipitated protein was dissolved to form a somewhat stronger solution, 0.13%. In this case the light absorption was that of about a 0.09% solution. The decomposition attending dilution thus appears to be at least in large part reversible.

A similar result was obtained when the reprecipitated, previously diluted hemocyanin was studied in the ultracentrifuge by the sedimentation velocity method. Precipitated hemocyanin obtained by the dialysis of a solution which had been only 0.03% for twenty-four hours was dissolved to form a solution of 0.127%. The light absorption of the non-centrifugible material corresponded to that of a solution about 17.5% as concentrated as that of the solution centrifuged. This was the value previously obtained in a solution of 0.09% (Table I). The effect of dilution was in this case partly reversed by the recombination which occurred during the dialysis, which resulted in the production of a precipitate of the original protein. In the cases in which the reversibility was not entirely complete it is probable that dialysis had not been continued for a sufficient time; the suspension removed from the bag and brought into solution by the addition of phosphate solutions may have been contaminated by some as yet uncombined material.



Pig. 4.

Discussion

Evidence has been presented from sedimentation velocity and equilibrium measurements in the ultracentrifuge and from measurements of the light absorption in the ultraviolet that a decomposition occurs in solutions of *Limulus* hemocyanin when diluted beyond 0.6%. The mechanism of the change (hydrolysis, disassociation or other type of splitting) has not been determined. The occurrence of such an effect of dilution upon the proteins is not unprecedented, for a similar change has been described in the case of serum albumin.[5] That the change occurs within the range of concentrations most suitable for the photographic recording of the motion of the protein in the centrifugal field complicates

---

[5] Svedberg and Sjögren, This Journal, 50, 3318 (1928).

greatly the molecular weight determination. If the mean of all of the diffusion constants obtained in each of the sedimentation velocity runs is employed in determining the molecular weight, a value of 1.60×10^6 results, which multiplied by 3.12 gives 4.99×10^6, a value very close to the molecular weight 5.08×10^6, which has been determined for the *Helix* hemocyanin. Such a comparison is perhaps possible because the error introduced by the mean drift in the diffusion constants with time is about that observed in the sedimentation of *Helix* hemocyanin at *P*H 4.7. It should, however, only be permissible to make such a comparison at either the isoelectric points of the two proteins or at regions so far removed from each of them that the ratio of charged to uncharged molecules is the same in each case. Only by so doing would it be possible to exclude the effects of the charges upon the ions which depress the diffusion constants, making the values of the molecular weights abnormally high. Since the reaction 6.63 employed in this work is probably less than 0.3 of a Sorensen unit alkaline to the isoelectric point, a comparison may be made of the molecular weight of the *Limulus* hemocyanin obtained by using only those diffusion constants free from drift, 2.04×10^6, with the apparent molecular weight of *Helix* hemocyanin at a PH 0.3 unit alkaline to its isoelectric point, or 5.5. If the values 1.90×10^6 or 2.04×10^6 are multiplied by 3.12 the values 5.93×10^6 or 6.36×10^6 are obtained. The apparent molecular weight of *Helix* hemocyanin at 5.62 has been found to be 6.19×10^6. The molecular weight of *Limulus* hemocyanin may then be stated to be, within the limits of experimental error, one-third that of the hemocyanin of *Helix.*

An attempt was made to calculate the diffusion constant for this protein by the aid of the Einstein equation

$$D = \frac{RT}{N} \times \frac{1}{6\pi r\eta}$$

in which R, T and N have their usual meanings and η is the viscosity of water at 20° expressed in absolute units. The radius, r, of the particle is calculated to be 8.398×10^{-7} from the molecular weight and density of the protein on the assumption that the molecules are spherical. As the mean value for the diffusion constant in those runs in which there was no drift with time was 0.0139, while the value obtained by the calculation outlined is 0.0214, it is evident that there is a large discrepancy. It is therefore probable that the assumption upon which the calculation was made, that is, that the molecules are spherical, is without justification. There is thus an analogy between these two hemocyanins and the proteins phycoerythrin and phycocyan. In each case the molecules of greater molecular weight are spherical. Phycocyan with half the molecular weight and the same diffusion constant as phycoerythrin and *Limulus* hemocyanin with one-third the molecular weight of *Helix* hemocyanin and a diffusion constant approximately that of the latter, each have molecules diverging widely from the spherical shape.

Summary

1. Measurements of the molecular weight of the hemocyanin of the horseshoe crab *Limulus polyphemus* have been made in dilute phosphate buffer solution at P_H 6.63 in concentrations of 0.03–0.09% of protein by the sedimentation velocity and the sedimentation equilibrium methods in the ultracentrifuge.

2. Both methods indicate that at concentrations of about 0.06–0.1% the protein undergoes decomposition.

3. The existence of this decomposition has been confirmed by measurements of the ultraviolet absorption, as the values of ϵ/c increase with dilution in this range of concentrations.

4. The decomposition is largely if not completely reversible and a protein of the same molecular weight and ϵ/c as that originally used may be precipitated from the dilute solutions by removing electrolytes by dialysis.

5. The sedimentation velocity method indicates for the hemocyanin of *Limulus polyphemus* a probable molecular weight of 2.04×10^6 under the conditions described.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE INFLUENCE OF THE HYDROGEN-ION ACTIVITY UPON THE STABILITY OF THE HEMOCYANIN OF HELIX POMATIA

BY THE SVEDBERG AND FRANCIS F. HEYROTH[1]

RECEIVED OCTOBER 2, 1928 PUBLISHED FEBRUARY 5, 1929

The previously reported determinations by ultracentrifugal methods[2] of the molecular weight of the hemocyanin isolated from the blood of the vineyard snail, *Helix pomatia*, were made upon solutions buffered to P_H 4.7, which is not far removed from P_H 5.2, the isoelectric point of the protein. This reaction was adopted to obviate the disturbing variation in the diffusion constant which in preliminary experiments at P_H 8.0 had been found to vary approximately inversely as the centrifugal force applied. As it was also noted that at P_H 3.8 the hemocyanin molecule appeared to break up into smaller units of undetermined size, a further study of this protein was deemed advisable in order to determine the region within which its huge molecules (of molecular weight 5,000,000 at P_H 4.7 in solutions containing 0.09% of protein) are stable. A similar series

---

[1] Fellow in Medicine of the National Research Council.

[2] Svedberg and Chirnoaga, THIS JOURNAL, 50, 1399 (1928).

of measurements of the molecular weight of carboxyhemoglobin[3] at various hydrogen-ion activities had indicated that protein to be stable over the range from *P*H 6.0 to 9.05.

Experimental

Material Used.—A suspension of dialyzed hemocyanin crystals prepared by Chirnoaga for the previously reported investigation and there described in detail was employed. The crystals were dissolved in 100 cc. of distilled water to form a 1.78% solution by the aid of only 1.5 cc. of an acetic acid–sodium acetate buffer of *P*H 4.7. Just before starting each of the centrifuging experiments, a 1:20 dilution was made from this stock solution into a buffer solution of the desired reaction. The buffers used were sodium acetate–acetic acid mixtures over the range of PH 5.62 and less, and mixtures of the primary and secondary sodium phosphates over the more alkaline range. In the former case the sodium-ion concentration was kept constant at 0.02 molar and the amount of acetic acid varied to give the required *P*H. In the case of the phosphate buffers, the ionic strength of the solution was maintained constant at 0.0225, the relative volumes of *M*/15 solutions of the two salts necessary to give the desired reactions being calculated by the method of Cohn.[4] In most cases the reported *P*H values were, however, determined electrometrically upon additional samples of the solutions prepared as for the actual runs. The concentration of the protein used was 0.089% in all except the runs at *P*H 3.8, in which it was somewhat higher. The value 0.738 at 20° was used for the partial specific volume in those few instances in which values for the molecular weight are reported.

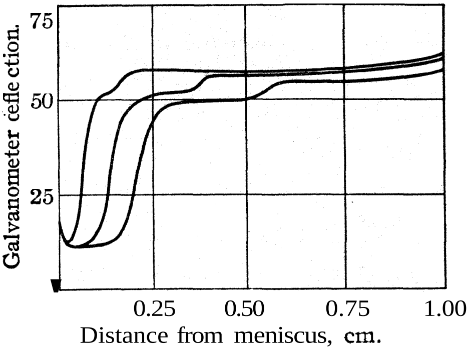


Fig. 1.

The material used contained a small quantity of a substance which moved in the centrifugal field somewhat more rapidly than the hemocyanin proper. This made itself evident by producing a second sedimentation boundary, appearing at the top of the usual concentration–distance curves, as shown in Fig. 1. This contamination in no way altered the sedimentation of the hemocyanin, as the heavier material was centrifuged down during the early part of each run. As may be seen from the results obtained at *P*H 4.7, reported in Table I, the specific sedimenta-

---

[3] Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927).

[4] Cohn, *ibid.*, 49, 173 (1927).

tion velocity and diffusion constant (and therefore molecular weight) checked very well with the values previously published and included in the table for comparison. For experiments made some months later upon the reversibility of the disintegration process to be described below, a fresh solution was employed, prepared by redissolving the precipitate obtained by redialyzing what remained of the former solution. This solution was free from the heavier material, so that in a run at P_H 4.7 only one boundary was observed.

The Determination of Molecular Weights.—The sedimentation velocity method was employed exclusively in this work. It is based upon the equation, $M = RTs/D(1 - V\rho)$, in which s is the specific sedimentation velocity or rate of movement of the boundary under unit centrifugal force in cm. per second, D is the diffusion constant of the protein in cm.^{2}/sec., V the partial specific volume of the protein, ρ the density of the solution, R the gas constant, and T the absolute temperature.[5] Except for the runs at P_H 3.8 and **3.9,** which were performed in the oil-turbine centrifuge operated at 42,000 and 25,000 r.p.m. (centrifugal force 102,000 and 36,000 times the force of gravity), respectively, the runs were all made at a speed of approximately 8400 r.p.m. (centrifugal force 4100 times the force of gravity) in a new ultracentrifuge designed for low and medium centrifugal fields.

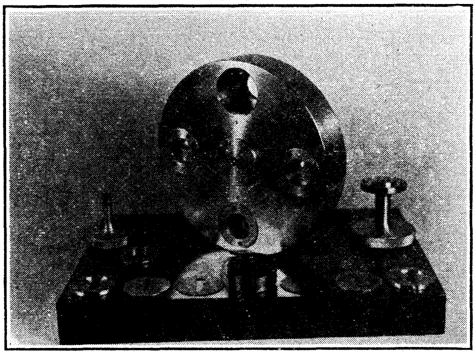


Fig. 2.

The cells employed were each made from two round quartz plates **30** mm. in diameter and **5** mm. thick, cemented to a third plate of the same diameter and 8 mm. thick. This had cut in it a sectorial aperture of 5°. The cell was cemented to a steel collar having an opening coincident with the opening of the sectorial cell. The steel collar containing the cell was supported by a system of sectorial disks and diaphragms in a hole drilled in the rotor of the centrifuge. Actually only a 3° sector was exposed to radiations passing through the cell when supported in the rotor. The latter, 15 cm. in diameter and **3** cm. in thickness, was arranged to receive four cells. In practice, however, only two cells were used at a time, the spaces for the other two being filled by aluminum blanks. Fig. **2** shows the rotor, one of the cells, and the various disks and diaphragms. The rotor was supported upon a vertical rotating shaft carrying two ball bearings, which in its turn was supported by a flexible steel rod. The energy of rotation was delivered by a motor and transferred to the rotating shaft by an endless screw device and a system of special couplings. To prevent heating the rotor was surrounded by hydrogen at atmospheric pressure, confined within a casing about the

---

[5] Svedberg and Nichols, THIS JOURNAL, 49, 2920 **(1927).**

rotor. To further ensure constancy of the temperature during each run the casing within which the rotor turned was immersed in a water thermostat regulated to maintain a temperature of 20° (Fig. **3**).

The casing of the centrifuge was also provided with two quartz windows, each fitted with an electromagnetic shutter. The optical system used is shown diagrammatically in Fig. 4. The ultraviolet radiations from a quartz mercury vapor lamp B, with matte surface for uniformity of illumination, mounted in a water-cooled lamphouse **A** were made to pass a 6-cm, water filter C, an 8-cm. bromine filter D, and an 8-cm. chlorine filter E. The radiations, which were thus restricted to those with wave lengths shorter than $290\mu\mu$,[6] were reflected vertically by the prism F through the cell I carried by the rotor H of the centrifuge G. The quartz lens K, of focal length **64.5** cm. and provided with an aperture of $f/25$, threw an image of the sectorial aperture in double natural size upon a photographic plate (Imperial Process) in a camera mounted in a room above that containing the centrifuge. The length of exposure was thirty seconds, except in two runs at PH *8.2* and **3.4,** in which shorter times were used.

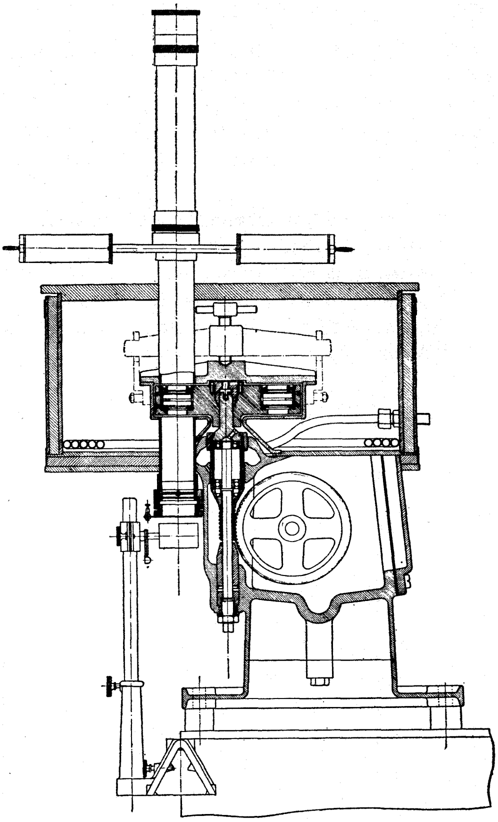


Fig. **3**.

Table I presents the results obtained in each of the runs. In it Col. 1 gives the PH, Col. 2 the specific sedimentation velocity and Col. **3** the diffusion constant, obtained from the blurring of the boundary. In Col. 4 are given molecular weights for those of the runs in which obvious disintegration of the molecules did not occur. The variation of s and D with PH is shown graphically in Fig. 5, dotted lines being employed in the regions in which disintegration is believed to have occurred.

Certain of the values for the "diffusion constant" are enclosed in parentheses to indicate that these values cannot be considered as representing the diffusion of molecules of uniform size. Table II and Fig. 6 illustrate the criterion by means of which it may be determined whether, in a given run, the concentration–distance gradients at the protein solution–solvent boundaries at successive time intervals may be ascribed entirely to the

[6] Svedberg and Nichols, THIS *JOURNAL*, 48, **3081 (1926).**

TABLE I

VARIATION OF SPECIFIC SEDIMENTATION VELOCITY AND DIFFUSION CONSTANT WITH P_H

P_H	s in cm./sec. × 10^{12}	D, diff. const., cm.²/day	M mol. wt. × 10^{-6}	P_H	s in cm./sec. × 10^{12}	D, diff. const., cm.²/day	M, mol. wt. × 10^{-6}
3.8	0.739	(0.0960)	...	4.7	8.55–10.3[a]	0.0140, 0.0165[b]	Mean 4.91
3.8[c]	0.574	(0.107)	...	5.62	9.79	0.0127	(6.37)
3.9A	0.765	(0.161)	...	6.3	9.79	0.0123	(6.44)
3.9B	6.01	(0.0068)	(7.1)	7.2	9.60	0.0166	(4.60)
4.1	6.66	(0.0503)	...	7.36	9.61	0.0123	(6.30)
4.3	9.23	(0.0315)	...	7.46[d]	9.43	0.0128	(6.03)
4.4	9.54	0.0174	...	7.65[d]	8.88	0.0299	....
4.5	9.88	0.0138	5.70	7.96'	7.99	0.0683	....
4.7	10.1	0.0155	5.24	8.0	2.09 est.	.....	....
				8.2[f]	8.24, 2.20	0.0196	....

[a] Mean, 9.42, determined by Chirnoaga.
[b] Mean, 0.0154.
[c] After 9 days.
[d] A trace of non-centrifugible substance.
[e] Slowly centrifuging and non-centrifuging substances.
[f] Much non-centrifugible material.

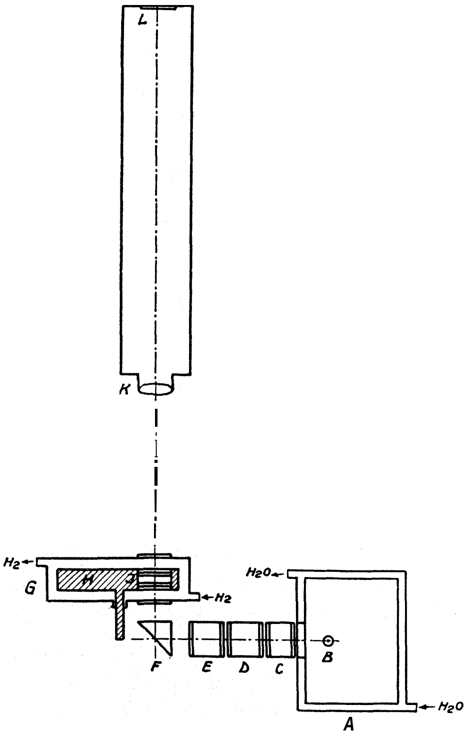


Fig. 4.

diffusion of the molecules against the force of centrifugation. If this is true, as is approximately the case, in Table II from P_H 4.5 to 7.46 the successive calculated values of D fluctuate about a mean which may be taken as the diffusion constant. If, however, the concentration-distance gradients at the boundaries are in part due to the increasing separation of molecules of not very different frictional resistances moving toward the bottom of the cell at different rates or moving downward at the same and diffusing backward at different rates, the successive calculated D values increase with some fluctuations throughout the run. It is the mean values of such runs (obtained at P_H values < 4.7 and > 7.46) which have been placed in parentheses, as they cannot be

TABLE II

"APPARENT DIFFUSION CONSTANTS" CALCULATED AT SUCCESSIVE THIRTY-MINUTE INTERVALS DURING EACH RUN

Acid to Isoelectric Point

	PH						
	4.7	**4.5**	**4.4**	**4.3**	**4.1**	**3.9**	**3.8**
1	0.0076	0.0062	0.0112	0.0076	0.0278	0.0095	0.0052
2	.0132	.0124	.0117	.0113	.0195	.0252	.0440
3	.0149	.0139	.0134	.0151	.0258	.0449	.0663
4	.0180	.0134	.0149	.0206	.0275	.0864	.184
5	.0156	.0125	.0160	.0278	.0407	.180	....
6	.0152	.0154	.0186	.0282	.0510	.214	....
7	.0158	.0130	.0221	.0486	.0608	.255	....
8	....	.0147	.0213	.0459	.0811	.321	....
9	....	.0155	.0215	.0548	.0967	.315	....
Mean[a]	.0155	.0138	.0174	.0312	.0503	.161	.107

Alkaline to Isoelectric Point

	PH						
	5.62	**6.3**	**7.2**	**7.36**	**7.46**	**7.65**	**7.9**
1	0.0076	0.0103	0.0089	0.0058	0.0103	0.0070	0.0111
2	.0116	.0110	.0081	.0116	.0105	.0152	.0127
3	.0127	.0134	.0209	.0128	.0114	.0153	.0174
4	.0118	.0130	.0167	.0099	....	.0210	.0303
5	.0144	.0104	.0173	.0140	.0129	.0263	.0568
6	.0151	.0117	.0166	.0133	.0140	.0246	.119
7	.0123	.0163	.0166	.0117	.0146	.0322	.103
8	.0145	.0127	.0192	.0124	.0136	.0475	.139
9	.0091	....	.0187	....	....	.0567	....
Mean	.0127	.0123	.0166	.0123	.0128	.0299	.068

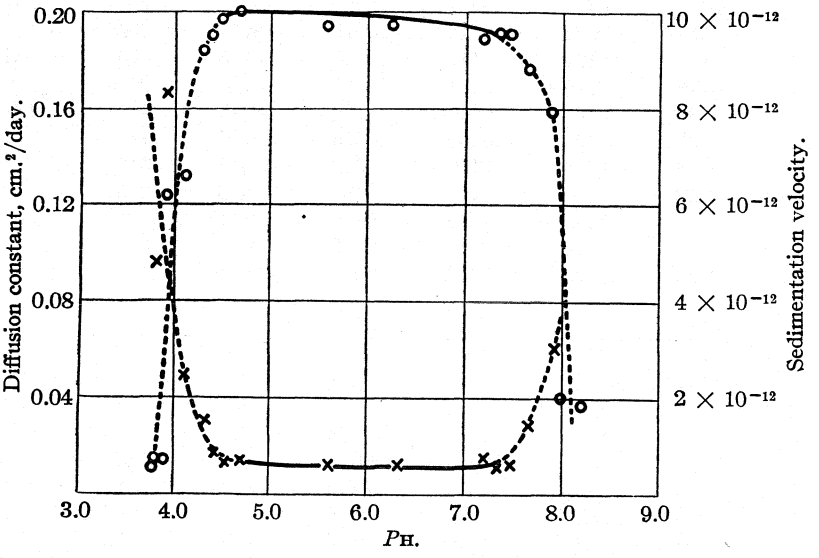
[a] In calculating the mean values the first value of each series was omitted, as during the first thirty minutes sedimentation had not progressed far enough to give a boundary from which the diffusion constant could be accurately obtained.

used for the calculation of molecular weights. In Fig. 6 lines have been drawn through the successive D values in three of the runs plotted on a scale which magnifies any drift: the slopes of the curves, plotting each in this manner (only three are given in Fig. **6** to avoid confusion), indicate a gradual loss of the uniformity of the molecules which exists near the isoelectric point as the solutions are made increasingly acid or alkaline. When the limits of the range **4.7–7.46** are exceeded, the slopes of such lines increase enormously. The increasing D values shown in the dotted portions of Fig. 5 are thus in large part due to this separation of unlike particles and in small part to the greater diffusibility of the smaller ones present.

Discussion of Results

Fig. 5 shows that the specific sedimentation velocity remains approximately constant at **9.61–10.00** × 10^{-12} between **PH 4.5** and **7.36;** at about these limits it decreases at first gradually and then very rapidly. The protein is thus stable between a reaction not greatly acid to its isoelectric point and one which corresponds approximately with that (7.4–7.8) believed to prevail in the snail's blood.[7]

The decrease in the rate of movement in the centrifugal field at reactions acid to PH 4.5 and alkaline to PH 7.36 may be regarded as indicating the presence of increasing numbers of smaller units resulting from a disintegration of the hemocyanin under the influence of the hydrogen or hydroxyl ions. The *s* values given on the descending dotted portions of the curve are therefore only to be regarded as mean sedimentation rates for mixtures in varying proportions of particles of various sizes. In support of the view that molecular disintegration occurs in these regions may be mentioned four experimental facts.



××××, diffusion; ○○○○, sedimentation.

Fig. 5.

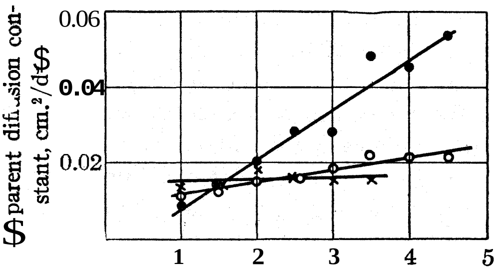


Fig. 6.

1. The previously mentioned drift in the apparent diffusion constants with time becomes enormous here.

2. The concentration–distance curves obtained during the early portion of a run at PH 3.9 and 25,000 r.p.m., shown (uncorrected for the sector shape of cell and for in-

---

[7] Duval, *Compt. rend.*, 179, 1629 (1924); Dambovicean u, *Compt. rend. soc. biol.*, 89, 261 (1923).

creased acceleration with distance) in Fig. **7**, exhibit two boundaries moving at different rates and corresponding to different particle sizes or to two mixtures each composed of particles not greatly unlike. A similar effect was noted in the two most alkaline runs.

3. Runs made with solutions which had been kept at *PH* 3.8 for differing periods of time give different values for the specific sedimentation velocity. The decrease with time suggests that the acid decomposition which is effected in large part very rapidly, continues at a lower rate. Thus *s* determined immediately after bringing the protein to *PH* **3.8** was **0.739** $\times 10^{-12}$. After nine days at this reaction, it decreased to 0.574 $\times 10^{-12}$.

4. The Tyndall cone is much diminished in intensity in the acid and alkaline solutions.

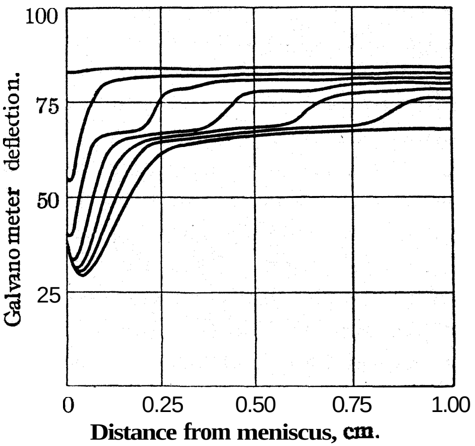


Fig. 7.

Our value of approximately 2.0 for *s* at *PH* 8.0 was much lower than the values **5.63–6.60** $\times 10^{-12}$ found in the previous investigation. An explanation is afforded by the run at *PH* 8.2, in which the form of the sedimentation curves indicated the presence of a small amount of material moving with a velocity *s* (8.24 X 10^{-12}) which is somewhat less than that of the protein, near its isolectric point, together with some material of *s* about 2.2 X 10^{-12}, and a large quantity of material non-centrifugible at 8000 r.p.m. The presence of the latter was indicated by the fact that the light absorption by the liquid between the protein boundary and the meniscus was much greater than that of the buffer solvent photographed in the same cell. It corresponded to that of a protein solution **40%** as concentrated as that (0.089%) used in the experiment. Solutions in the neighborhood of *PH* **8.0** thus appear to contain particles the sizes of which are distributed about three

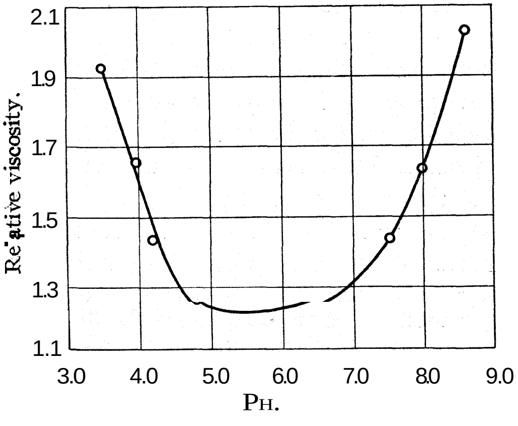


Fig. 8.

values. The relative amounts of the material in each of these magnitudes appears to vary rapidly with time and slight alterations in P_H. The s values on the alkaline side are somewhat less reproducible than those on the acid side of the stability region.

In Fig. 8 is reproduced the curve obtained by Stedman and Stedman[8] for the relation of the viscosity of the dialyzed serum of the snail, *Helix,* to the P_H. The curve shows increases in the relative viscosity amounting almost to double, in exactly those P_H regions in which the specific sedimentation velocity falls off most sharply. These investigators furnish no measurements between P_H 4.7 and 7.3. It might at first be supposed that the increased viscosity retards the movement of the protein under the centrifugal field. It is, however, the viscosity of the solvent and not that of the protein solution as such which is believed to influence the rate of centrifugation. Even though this were not the case, the viscosity changes in the dilute solutions employed would be insufficient to account for the observed drop in the sedimentation velocity.[9] The rising values for the diffusion constant in these regions would be entirely inexplicable upon such a supposition. Sufficient independent evidence has also been presented to indicate that a disintegration of the molecules actually occurs in these regions.

It is therefore possible that, on the other hand, the dispersion of the protein into smaller units may have been in part at least responsible for the increase in viscosity observed by Stedman and Stedman. An increase in the viscosity of sulfur sols attending a diminution in the size of the particles present has been noted by Odén.[10]

To the suggestion of Pauli[11] that the increased viscosity of the solutions of proteins away from their isoelectric points is due to increased hydration accompanying the formation of the protein ions, may be added, at least in the case of hemocyanin, the possibility that it may be in part due to the increase in dispersion resulting from a disintegration of the molecules. The analysis by Smoluchowski[12] of the limits of applicability of the Einstein equation for the variation of the viscosity of a colloidal suspension with its volume concentration indicates that it may only be expected to hold when, among other conditions, the ratio of the particle radius to the distance between the particles is small. As in snail blood the diameter of the hemocyanin molecules is about two-thirds the distance between the

---

[8] Stedman and Stedman, *Biochem. J.,* 21, 541 (1927)

[9] The non-centrifugible material present at P_H 8.0 may, however, be considered to be a portion of the solvent within which the heavier units are moving, and the increase in viscosity which its presence imparts to the buffer solution may aid in lowering the sedimentation rate of the larger unattacked or partly disintegrated molecules.

[10] Odén, *Nov. Act. Reg. Soc. Scient. Upsala,* [4] 3, 85 (1913).

[11] Pauli, *Kolloid-Z.,* 40, 185 (1926).

[12] Smoluchowski, *ibid.,* 18, 190 (1916).

surfaces of the adjacent molecules, the Einstein equation need not be expected to apply to viscosity changes in the serum studied by Stedman and Stedman, and accordingly its implication that the degree of dispersion of the particles is without influence upon the viscosity need not be binding.

The determination of the magnitudes of the particles formed by the acid or alkaline disintegrations of the hemocyanin must be postponed until greater centrifugal fields are available. The results of sedimentation experiments at 42,000 r.p.m. indicate that even at PH 3.8 all of the light-absorbing material present occurs in particles of size sufficient to move measurable distances in the short times within which runs are completed, since the light absorption in that portion of the liquid between the protein boundary and the meniscus corresponds to that of the pure buffer employed as solvent. This appears to exclude the possibility that the acid decomposition proceeds far enough to result in the formation of amino acids, the motion of which would not be measurable under the conditions described. The light-absorbing units which result from the alkaline disintegration are not, however, as completely removed from that part of the liquid from which most of the protein molecules have been centrifuged. Small amounts of such non-centrifugible material were noted in every run made at a *PH* greater than 7.4, so that it is probable that the disintegration induced by hydroxyl ions proceeds somewhat further than that due to hydrogen ions.

The **Reversibility** of the Disintegrations.—Some months after the conclusion of these experiments a number of additional runs were made to determine whether or not the acid breakdown of the hemocyanin is reversible. Crystals freshly dialyzed from the remainder of the stock solution used in the earlier experiments were dissolved by the addition of a small amount of buffer solution to form a stock solution containing 1.66% of protein at *PH* 4.7. When diluted to 0.087%, this was found free from material non-centrifugible at 8000 r.p.m., and its specific sedimentation velocity checked well with that previously obtained. One of the runs was made at *PH* 3.4, attained by adding only the acid of the acetic acid–sodium acetate buffer required to make a similar dilution at *PH* 4.7. At 8000 r.p.m. only a small fraction of the light-absorbing material present underwent sedimentation, and this at a rate which could be only roughly estimated as 0.8 that of the hemocyanin in its stable region. The light absorption in the region which might be expected to contain only buffer solution corresponded instead to that found in *a* solution containing 52% of the protein present in the solution used. Another sample which had stood at PH **3.4** for about eight hours was brought to *PH* 4.7 by the addition of the requisite amount of sodium acetate. The Tyndall cone, which had not been entirely destroyed by the acid treatment, was markedly increased in intensity and a small amount of a coarse precipitate was produced at the same time. After several hours, a run showed the presence of non-centrifugible material corresponding in light absorption to a solution containing but 19% (21% in a second experiment) of the amount of hemocyanin in the original solution, indicating that the acid decomposition had been partly reversed. In a third experiment, in which the acid treatment was maintained for only one hour before restoring the PH to 4.7, a large proportion of molecules of the original size were reformed, and the amount of non-centrifugible material was correspondingly less, as the light absorption equaled that of a solution of 12% of the original protein concentration. In all three of these experiments the forms of the sedimentation curves indicated the presence of smaller particles in admixture. It thus appears that the first products which result from the acid-induced decomposition of the hemocyanin may reunite when the solution is restored to PH values at which it is stable. Such a process is attended by some loss of material by precipitation and is never quite complete. On maintaining the acid reaction for longer periods a further irreversible splitting appears to ensue.

The Region of Stability.—At PH 4.7[13] both the specific sedimentation velocity and the diffusion constant have maximal values. As the PH is made increasingly acid to this or increasingly alkaline beyond the isoelectric point, both of these values decrease progressively and gradually. This effect may possibly be explained as due to progressively increasing hydration of the protein molecules under the influence of the acid or alkali. The theoretical effect of hydration would be a lowering of both the specific sedimentation velocity and the diffusion constant by the same fraction of their values for material at the isoelectric point. Calculations showed that the new values to be expected were each of the molecules covered by a monomolecular layer of water, would be in the neighborhood of 97.4% of the corresponding values at the isoelectric point. The decreasing values of s (Table I), as the PH values at which decomposition occurs are approached, are, within the limits of accuracy of these measurements, in accord with the supposition that the decomposition of the molecules is preceded by their hydration.

The diffusion constants also diminish from the region of the isoelectric point to the regions of beginning decomposition. The decrease is, however, greater than that of the sedimentation velocity. This discrepancy is somewhat obscured by the fact that even in this region there is a slight and gradually increasing drift in the diffusion values obtained at successive time intervals. Thus each of the mean values plotted in Fig. 5 is slightly too great, the errors increasing as the regions of decomposition are approached. This excess diminution of the diffusion constants over that

---

[13] As this series of measurements was completed before it was learned that the isoelectric point of the protein is *5.2,* no run was performed at that PH.

to be expected as the result of hydration, while apparently slight, is nevertheless sufficient to lead to relatively great errors (20%) in the molecular weights calculated by their aid. The diminution in the diffusion may possibly be explained as due to the mutual interaction of the charges upon the ions which are formed in increasing relative amounts as the reaction is brought away from the isoelectric point. The great size and therefore proximity of the ions would render such an effect likely. Such interionic forces would not alter the rate of sedimentation of the molecules and ions as a group. In this respect they would be analogous to or identical with the forces postulated in the previous communication to account for the diminished diffusion and only slightly diminished sedimentation rate observed in hemocyanin solutions at *P*H 4.7 as the concentration of the protein is increased. The diminution of diffusion resulting from the presence of charged ions in close proximity tends to obscure itself in the graphical records of the sedimentation of the protein, as it may itself be in part responsible for the slight drift with time in the diffusion values obtained in this region. The greater diffusibility of the uncharged molecules over that of the ions would tend to cause an increase in the blurring of the boundary with time.

Summary

1. The variation of the specific sedimentation velocity and the diffusion constant of the hemocyanin of Helix *pomatia* have been measured over the range of PH from 3.8 to 8.2.
2. Hemocyanin in 0.089% concentration in dilute acetate and phosphate buffer solutions from PH 4.5 to 7.4 possesses a molecular weight of five million.
3. As these limits of PH are approached, the protein molecules become hydrated and as the limits are exceeded rapidly undergo disintegration into smaller particles of undetermined magnitude.
4. The acid disintegration is in its earliest stages reversible, but the disintegration of the products first formed continues slowly and is in its later stages irreversible.
5. The *P*H ranges within which the disintegration occurs are the same as those within which the viscosity of snail serum is known to increase rapidly.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE LABORATORIES OF HYNSON, WESTCOTT AND DUNNING AND THE UNIVERSITY OF MARYLAND]

A NEW SERIES OF SULFONEPHTHALEINS

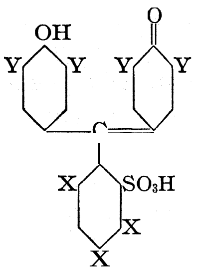
BY WILTON C. HARDEN WITH NATHAN L. DRAKE

RECEIVED OCTOBER 4, 1928 PUBLISHED FEBRUARY 5, 1929

The sulfonephthaleins together with the phthaleins constitute a group of compounds that has long been of much interest. Since the synthesis of the first members of the former class by Remsen and his co-workers,[1] they have been extensively used both as indicators and as diagnostic aids in clinical and experimental medicine. Orndorff and his students,[2] Clark and Lubs,[3] Cohen[4] and others have made important contributions to this field of chemistry.

The sulfonephthaleins, in general, and phenolsulfonephthaleins in particular, have been much used as a means of testing the renal function, since they are eliminated from the blood stream after intravenous injection almost quantitatively through the kidneys.[5] Those phenolphthaleins, on the other hand, which contain four halogens in the phthalic acid residue are eliminated from the blood stream through the liver and hence are used as tests of hepatic function.[6]

Having these facts in mind, it was thought that a study of the chemical behavior and pharmacological action of those sulfonephthaleins having four halogens in the o-sulfobenzoic acid part of the molecule would be of interest. The recent synthesis of the di- and tetra-halogenated o-sulfobenzoic acids and their anhydrides by Twiss[7] has made possible the preparation of such a series of compounds. The purpose of the present paper is to describe a limited number of compounds of this class. Their general formula may be represented as shown in the accompanying diagram, where X is any halogen and Y may be hydrogen or halogen.



No attempt has been made to prepare all the possible members of this class, the authors having been content to limit themselves to the following compounds: phenoltetrachlorosulfonephthalein, phenoltetrabromosulfonephthalein, o-cresoltetrachlorosulfonephthalein, *o*-cresoltetrabromosulfone-

---

[1] (a) Remsen, *Am. Chem.* J., 6, 180 (1884); (b) Remsen and Saunders, *ibid.*, 17, 352 (1895); (c) Sohon, *ibid.*, 20,257 (1898).

[2] (a) Orndorff and Sherwood, THIS JOURNAL, 45, 486 (1923); (b) Orndorff and Shapiro, *ibid.*, 46,2856 (1924), and others.

[3] (a) Clark and Lubs, J. *Wash. Acad. Sci.*, 5,609 (1915); (b) 6,481,483 (1916).

[4] (a) Cohen, *U.* S. *Pub. Health Reports*, 38, 199 (1923); 41, (b) 53, (c) 3015 (1926).

[5] Rowntree and Geraghty, J. *Pharmacol.*. 1, 579 (1910).

[6] (a) S. M. Rosenthal, J. *Pharmacol.*, 24, 385 (1922); (b) Rosenthal and White, *J. Am. Med. Assocn.*, 84, 1112 (1925).

[7] Twiss, U. S. Patent Application No. 267,473, filed April 4, 1928.

phthalein, tetrabromophenoltetrabromosulfonephthalein, tetrabromophenoltetrachlorasulfonephthdein, dibromo-*o*-cresoltetrabromosulfonephthalein, dibromo-o-cresoltetrachlorosulfonephthalein, dibromophenoltetrabroinosulfonephthalein and o-cresoltetra-iodosulfonephthalein. Phenoltetra-iodosulfonephthaleinhas also been prepared but is not included in the present investigation. In naming these compounds the author has adopted the usual custom, that is, halogen preceding the phenol indicating its presence in the phenolic part of the molecule and halogen following the phenol indicating its presence in the o-sulfobenzoic acid part.

Experimental Part

Preparation of **Phenoltetrachlorosulfonephthalein.**—Eleven g. of phenol was heated to 110° in a small three-necked flask; 16.1 g. of tetrachloro-*o*-sulfobenzoic acid anhydride was then added and the mixture stirred until all had dissolved. Eight cc. of fuming stannic chloride was then added and the temperature raised to 120–130°. Heating was continued at this temperature for eight hours, with mechanical stirring. The melt was then poured into water and steam distilled to remove excess phenol. After distillation the dye solution was made alkaline with sodium carbonate and allowed to stand overnight. It was then filtered to remove the precipitated tin and poured into 1:1 hydrochloric acid with rapid mechanical stirring. The crude dye was thus precipitated as a red or pink amorphous powder. It was filtered off, redissolved in sodium carbonate, filtered and again precipitated with hydrochloricacid; yield, 11 grams (45%). A small portion was then crystallized from hot benzene, in which it is difficultly soluble, dried and analyzed.

Anal. Calcd. for $C_{19}H_{10}O_5Cl_4S$: Cl, 28.85; S, 6.50. Found: Cl, 28.64; S, 6.58.

Preparation of **Tetrabromophenoltetrachlorosulfonephthalein.**—Four and nine-tenths g. of crude phenoltetrachlorosulfonephthalein prepared as described above was suspended in 50 cc. of glacial acetic acid. A slight excess over the calculated amount of bromine dissolved in glacial acetic acid was introduced through a dropping funnel while the suspension was stirred mechanically. The suspended dye slowly dissolved upon addition of the bromine and when all had been added the flask was allowed to stand uncorked at room temperature overnight. A small crop of crystals settled out; these were filtered off, the solution wsa warmed on a water-bath and the hydrobromic and some of the acetic acid removed by passing a current of air through the solution. When the solution had been reduced to about half its original volume, the flask was stoppered and allowed to cool in the ice box. The brominated dye crystallizes as salmon-colored crystals; yield 6.5 (81%). After two recrystallizations from acetic acid a sample analyzed as follows.

Anal. Calcd. for $C_{19}H_6O_5Cl_4Br_4S$: Cl, 17.56; Br, 39.58; S, 3.96. Found: Cl, 17.10; Br, 39.90; S, 3.61.

Preparation of **Phenoltetrabromosulfonephthalein.**—Fifteen *g.* of phenol was heated in an oil-bath for half an hour at 110°, 25.85 g. of the anhydride of tetrabromo-*o*-sulfobenzoic acid was added, the mixture well stirred, 8 cc. of fuming stannic chloride added and the mixture heated to 130–140° for seven hours. The solid melt thus obtained was subjected to steam distillation, treated with sodium carbonate and hydrochloric acid as in the case of the tetrachloro compound, dried and weighed; yield, 20 g. (60%). A small portion was repeatedly recrystallized from hot benzene as before.

Anal. Calcd. for $C_{19}H_{10}O_5Br_4S$: Br, 47.70; S, 4.70. Found: Br, 47.56; S, 4.55, 4.71.

Preparation of **Tetrabromophenoltetrabromosulfonephthalein.**—Six and seven-tenths g. of the phenoltetrabromosulfonephthalein prepared as above was suspended in **50** cc. of glacial acetic acid, and **7** g. of bromine in **20** cc. of glacial acetic acid was added slowly with constant stirring. The solution was allowed to stand at room temperature overnight; hydrobromic acid was then removed by a current of air, the solution cooled, filtered, the cream-colored crystals recrystallized twice from acetic acid, dried at 80° and analyzed.

Anal. Calcd. for $C_{19}H_6O_5Br_8S$: Br, **64.77;** S, **3.23.** Found: Br, **64.68, 64.48; S, 3.41, 3.40.**

Preparation of **o-Cresoltetrachlorosulfonephthalein.**—Twelve g. of o-cresol was heated just as in the previous condensations, and **16.1** g. of the anhydride of tetrachloro-o-sulfobenzoic acid added. No condensing agent was used, previous experience having shown it to be unnecessary in most condensations with o-cresol. The mixture was heated for two hours at **120–130"** and then the temperature was slowly raised (one hour) to 160° and maintained at this point for an additional two hours. Purification was carried out as in previous condensations, the crude dye being crystallized from hot benzene in greenish-red iridescent plates; yield, **19** g. **(73%).** After one recrystallization, analysis gave the following results.

Anal. Calcd. for $C_{21}H_{14}O_5Cl_4S$: Cl, 27.27; S, **6.15.** Found: **Cl, 27.16;** S, **6.14.**

Preparation of **Dibromo-o-cresoltetrachlorosulfonephthalein.**—Six g. of o-cresoltetrachlorosulfonephthalein prepared as above was suspended in **50** cc. of glacial acetic acid and the calculated amount of bromine in glacial acetic acid added as before. In several minutes a large crop of white crystals had formed. On standing overnight in the ice box another portion crystallized out. The portions were united and recrystallized three times from acetic acid.

Anal. Calcd. for $C_{21}H_{12}O_5Br_2Cl_4S$: Br, **23.57; Cl, 20.92;** S, **4.72.** Found: Br, **23.92; Cl, 20.61;** S, **4.74.**

Preparation of **o-cresoltetrabromosulfonephthalein.**—The condensation was carried out as in the case of the o-cresoltetrachloro compound, using **14** g. of o-cresol and **25** g. of the anhydride of tetrabromo-o-sulfobenzoic acid; yield, **28** g. **(82%).** Repeated crystallization from benzene gave a product which analyzed as follows.

Anal. Calcd. for $C_{21}H_{14}O_5Br_4S$: Br, **45.80;** S, 4.58. Found: Br, **45.48;** S, **4.56.**

Preparation of **Dibromo-o-cresoltetrabromosulfonephthalei—Foe** g. of the material just described was suspended in **100** cc. of glacial acetic acid, the calculated amount of bromine in glacial acetic acid added and the mixture treated as in previous brominations. In this case, however, crystallization from acetic acid did not give a pure product, so the crystals were dissolved in a small amount of hot acetone, **5** g. of "Norite" and **2** cc. of acetic acid added and the mixture boiled for one hour under a reflux condenser. The solution was then filtered while hot and concentrated by evaporation on the water-bath. The dye came out as a pink amorphous powder, which was dried and again crystallized from acetic acid. By this method a product giving the following analysis was obtained.

Anal. Calcd. for $C_{21}H_{12}O_5Br_6S$: Br, **56.03;** S, **3.73.** Found: Br, **56.12;** S, **3.65.**

Preparation of **o-Cresoltetra-iodosulfonephthalein.**—Eighteen g. of o-cresol was heated in an oil-bath to 110–120° and **20** g. of tetra-iodo-o-sulfobenzoic acid anhydride was added and the mixture well stirred. Ten cc. of stannic chloride and **0.5** cc. of sulfuric acid were then added and the mixture heated at 120–130° for five hours, being stirred mechanically. The melt was then poured into water and steam distilled to remove excess cresol. The crude dye was then repeatedly dissolved in dilute sodium hydroxide and precipitated by hydrochloric acid. A small fraction was recrystallized several times from acetic acid, in which it is only slightly soluble.

And. Calcd. for $C_{21}H_{14}O_5I_4S$: I, 57.32; S, 3.61. Found: I, 57.25; S, 3.61,

Preparation of Dibromophenoltetrabromosulfonephthalein.—Twenty g. of o-bromophenol (Eastman) was heated at 110° and 26 g. of tetrabromo-o-sulfobenzoic acid anhydride was added. When the anhydride had completely dissolved, 5 cc. of stannic chloride was added and the temperature raised to 120–130° and kept at this point for twelve hours. Excess bromophenol was removed by steam distillation and the dye partially purified by repeated solution in sodium carbonate and precipitation by means of hydrochloric acid. The dye is very soluble in water and appreciably soluble in dilute hydrochloric acid. A small sample was crystallized from acetic acid and analyzed.

Anal. Calcd. for $C_{19}H_8O_5Br_6S$: Br, 58.90; S, 3.86. Found: Br, 58.69; S, 3.91.

Discussion

Since the unhalogenated analogs of all these compounds are useful indicators for the determination of hydrogen-ion concentration, it was thought that a study of the useful P_H range of these compounds would be of value. The method employed in each case was as follows: 0.1 g. of the dye was thoroughly ground in a small glass mortar with sufficient *N*/20 sodium hydroxide to form the monosodium salt. The resulting solution was diluted to 250 cc. to give a 0.04% aqueous solution of the sodium salt.[8] One-half cc. of this solution was then added to 10 cc. of various buffers from P_H 1.0 to 9.6 and the color ranges carefully observed. The indicators were found to have the ranges and colors shown in the accompanying table (Table I).

TABLE I

COLOR CHANGE AND USEFUL Pa RANGE OR TETRAHALOGENATED SULFONEPHTHALEINS

Name	P_H interval	Color change
Phenoltetrabromosulfonephthalein	6.6 to 8.2	Yellow to purple
Phenoltetrachlorosulfonephthalein	6.6 to 8.2	Yellow to purple[a]
o-Cresoltetrabromosulfonephthalein	7.2 to 8.8	Yellow–violet–purple
o-Cresoltetrachlorosulfonephthalein	7.2 to 8.8	Yellow–violet–purple
Tetrabromophenoltetrabromosulfonephthalein	3.0 to 4.6	Yellow–green–blue
Tetrabromophenoltetrachlorosulfonephthalein	3.0 to 4.6	Yellow–green–blue[a]
Dibromo-o-cresoltetrabromosulfonephthalein	5.2 to 6.8	Yellow–green–violet
Dibromo-o-cresoltetrachlorosulfonephthalein	5.2 to 6.8	Yellow–green–violet[a]
Phenoltetra-iodosulfonephthalein (crude)	6.4 to 8.0	Yellow to red
o-Cresoltetra-iodosulfonephthalein	7.0 to 8.6	Yellow to purple
Dibromophenoltetrabromosulfonephthalein	5.6 to 7.2	Yellow to purple

[a] Lighter shades.

Table II shows the useful P_H interval of their unhalogenated analogs. A study of the two tables brings out some very interesting facts. The nature of the halogen in the o-sulfobenzoic acid part seems to affect the color only very slightly. The only difference is that in the case of the chlorine compounds the shades are somewhat lighter. A more important

---

[8] Clark and Lubs, "Determination of Hydrogen Ions," Williams and Wilkins Company. Baltimore, Maryland, 1922, 2nd ed.

observation, however, is that the replacement of four hydrogens in the *o*-sulfobenzoic acid part of the molecule by halogens does not materially change the useful PH range of the compounds. In each case the useful range is practically the same for the two series, although the colors are somewhat different. The halogenated compounds show an additional extremely acid range not measurable by the ordinary buffers. This range might possibly prove useful since in strong acid (N HCl) they are red shading to yellow at *P*H's in the vicinity of 2.0.

TABLE II[a]

COLOR CHANGE AND *P*H RANGE OF THE UNHALOGENATED ANALOGS OF THOSE COMPOUNDS SHOWN IN TABLE I

Name of indicator	Trade name	Concn., %	Interval in *P*H	Color	
				Acid	Alkaline
Phenolsulfonephthalein	Phenol red	0 02	6.8–8 6	Yellow	Red
Tetrabromophenolsulfonephthalein	Brom phenol blue	.04	3.0–4.6	Yellow	Blue
o-Cresolsulfouephthalein	Cresol red	.02	7 2–8.8	Yellow	Red
Dibromo-o-cresolsulfonephthalein	Brom cresol purple	.04	5.2–6 8	Yellow	Purple

[a] Adapted from Kolthoff and Furman, "Indicators," John Wiley and Sons, Inc., New York, 1928.

The effect of halogen and alkyl substitution in the phenolic part of the molecule as shown in Table I is identical with that observed by other investigators.[3a,4c] in the unhalogenated series.

The new compounds show the usual dichromatism found in so many of the sulfonephthaleins and possess no apparent advantage as indicators over those now in general use. No attempt has been made to determine the apparent dissociation constants of these compounds nor any spectrophotometric data regarding them.

The author wishes to express his thanks to Mr. Grant Spurrier of the Research Laboratories of Hynson, Westcott and Dunning for his technical assistance.

Summary

1. The following compounds have been prepared: phenoltetrabromosulfonephthalein, phenoltetrachlorosulfonephthalein, *o*-cresoltetrabromosulfonephthalein, o-cresoltetrachlorosulfonephthalein, *o*-cresoltetra-iodosulfonephthalein, tetrabromophenoltetrabromosulfonephthalein, dibromophenoltetrabromosulfonephthalein, tetrabromophenoltetrachlorosulfonephthalein, dibromo-o-cresoltetrabromosulfonephthalein and dibromo-*o*-cresoltetrachlorosulfonephthalein.

2. Their color change with changing hydrogen-ion concentration has been determined.

3. Their pharmacological and bacteriological action is being investigated and will be reported elsewhere.

4. Further investigation of compounds of this series is in progress.

BALTIMORE AND COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

THE FORMATION OF PRIMARY AMINES FROM GRIGMARD REAGENTS AND MONOCHLORO-AMINE. II

BY GEORGE H. COLEMAN AND CHARLES B. YAGER

RECEIVED OCTOBER 11, 1928 PUBLISHED FEBRUARY 5, 1929

In a recent[1] study of the reaction of monochloro-amine with Grignard reagents, it was found that primary amines and ammonia are formed according to the following reactions

$$RMgX + NH_2Cl = RNH_2 + MgXCl \qquad (1)$$

$$RMgX + NH_2Cl = RCl + MgXNH_2 \qquad (2)$$

The reagents used, with the exception of phenylmagnesium chloride, bromide and iodide, were prepared from primary halogen compounds.

Since some of the methods used for the preparation of primary amines cannot be used for amines in which the amino group is attached to a secondary or a tertiary carbon atom, the monochloro-amine reaction has been studied with Grignard reagents prepared from secondary and tertiary halogen compounds. The course of the reaction and the yields of amines and ammonia are much the same as with the primary reagents. The variation in yields with chlorides, bromides and iodides was again observed. The results obtained with the fifteen reagents thus far used are shown in Table I.

TABLE I

PERCENTAGE YIELDS OF AMINES AND AMMONIA FROM MONOCHLORO-AMINE AND GRIGNARD REAGENTS

	X = Cl % yields		X = Br % yields		X = I % yields	
Reagents	RNH_2	NH_3	RNH_2	NH_3	RNH_2	NH_3
Iso-C_3H_7MgX	65.5	29.5	37.2	54.7	9.0	79.0
Sec.-C_4H_9MgX	70.0	20.0	51.1	38.9	15.8	74.13
Sec.-$C_5H_{11}MgX$[a]	71.7	19.0	31.6	61.9	13.7	79.13
Tert.-C_4H_9MgX	60.2	39.0	20.24	79.7	4.8	81.4
Tert.-$C_5H_{11}MgX$	66.2	30.9	14.25	79.2	2.0	80.2

[a] The secondary amyl halides used were the symmetrical compounds prepared from diethylcarbinol.

The monochloro-amine was prepared by a further slight modification of the method of Marckwald and Wille.[2] Instead of distilling the aqueous solution under diminished pressure the monochloro-amine was extracted directly with ether.

Since it was essential to have an excess of Grignard reagent present, the organomagnesium halide solutions were analyzed by titration with

---

[1] Coleman and Hauser, THIS JOURNAL, 50, 1193 (1928).

[2] Marckwald and Wille, Ber., 56, 1319 (1923).

acid as described by Gilman, Wilkinson, Fishel and Meyers[3] before adding the monochloro-amine.

The method of carrying out the reaction and isolating the products was very similar to that described by Coleman and Hauser.[1] The products obtained as the amine hydrochlorides and ammonium chloride were analyzed and derivatives prepared.

Work is being continued with other chloro-amines and with nitrogen trichloride with the thought of preparing secondary and tertiary amines. The work of Buylla[4] with iododiethylamine and Strecker[5] with nitrogen trichloride might indicate, however, that Reaction *2* predominates in these cases.

Experimental

Preparation of Monochloro-amine.—Two hundred cc. of cold sodium hypochlorite solution prepared as described by Marckwald and Wille[2] was added slowly with shaking to 200 cc. of 1 *N* ammonium hydroxide cooled to 0° or below. The monochloro-amine was extracted first with a 100-cc. portion of cold ether and then with three 50-cc. portions. The four extractions were combined and dried for a short time with calcium chloride. The yield of monochloro-amine by this method is somewhat less than that obtained by the distillation method described by Coleman and Hauser[1] using carbon dioxide snow around the receiver. The method is, however, much simpler and the yield is better than by the distillation method if the receiver is cooled with only ice and salt.

Analysis of the Monochloro-amine Solution.—The method used was that previously described[1] with a slight modification of procedure in the analysis for nitrogen. After adding the sample to the hydrochloric acid, the flask was stoppered and shaken vigorously for a short time. It was then opened and the chlorine and ether driven off by gentle warming. With the dilute solutions used the results were as satisfactory as those obtained by allowing the hydrochloric acid mixture to stand for several hours. For concentrated solutions of monochloro-amine the method used by Coleman and Craig[6] for concentrated solutions of nitrogen trichloride may be used.

Preparation of the Grignard Reagents.—The methods used in the preparation and analysis of the Grignard reagents were essentially those described by Giman and his co-workers.[3,7]

Reaction of Monochloro-amine with Grignard Reagents

The reactions of monochloro-amine with the Grignard reagents were carried out as previously described.[1] After the excess Grignard reagent had been decomposed with water, however, the basic mixture was always brought into solution with acid before adding alkali and distilling with steam.

The purity of the hydrochloride was determined by analysis and the amines were identified by the preparation of derivatives. Mixed melting points were taken with known compounds when these were available.

---

[3] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45,150 (1923).

[4] Buylla, *Rev. real. acad. cien. Madrid,* 9,635–653, 718–734 (1910).

[5] Strecker, *Ber.,* 43, 1133 (1910).

[6] Coleman and Craig, THIS JOURNAL, 50, 1816 (1928).

[7] Gilman and Meyers, *ibid.*, 45, 159 (1923); Gilman and Zoellner, *ibid.,* 50, 425 (1928).

Benzoyl-*tert.*-amylamine.—The benzoyl derivative was prepared from the amine hydrochloride by the Schotten-Baumann method. After recrystallization from ligroin the melting point was 93–94° (uncorr.).

Anal. Subs., 0.1982, 0.1617: 10.4, 8.49 cc. of 0.1 N HCl. Calcd. for $C_{12}H_{17}ON$: N, 7.33. Found: 7.34, 7.35.

Summary

The yields of amines and ammonia in the reaction of monochloro-amine with Grignard reagents prepared from secondary and tertiary halogen compounds are much the same as with reagents prepared from primary halogen compounds.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 595]

FURTHER STUDIES OF SYRINGIC ACID AND ITS DERIVATIVES[1]

BY MARSTON TAYLOR BOGERT AND BERNARD B. COYNE[2]

RECEIVED OCTOBER 13, 1928 PUBLISHED FEBRUARY 5, 1929

In previous articles[3] from these Laboratories, we have described various derivatives of syringic acid and incidental compounds, and the present paper continues and supplements these earlier investigations.

The flow sheet represents the various products prepared in the course of the work and the origin of each.

The nitration of polyhydroxylated benzoic acids is complicated by the tendency of such compounds either to undergo complete decomposition, or to have the carboxyl displaced by the nitro group.[3a,4] These tendencies have been overcome by protecting the carboxyl group by esterification and the hydroxyls by alkylation or esterification.[3a,5] Bogert and Plaut[3a] obtained the dinitropyrogallol dimethyl ether by direct nitration of syringic acid. We have found similarly that when nitrosyringic acid is boiled with tin and hydrochloric acid, the product is the monaminopyrogallol dimethyl ether, but that the aminosyringic acid can be obtained by carrying out the reduction at 40–45° under suitable conditions.

Schiffer[6] encountered similar difficulties when he sought to reduce nitrotriethylgallic acid. We have also ascertained, in line with the above, that acetylsyringic acid can be nitrated easily, in acetic anhydride solution, to give the nitro-acetylsyringic acid without loss of carbon dioxide

---

[1] Presented in abstract before the Division of Organic Chemistry at the Swampscott Meeting of the American Chemical Society, September, 1928.

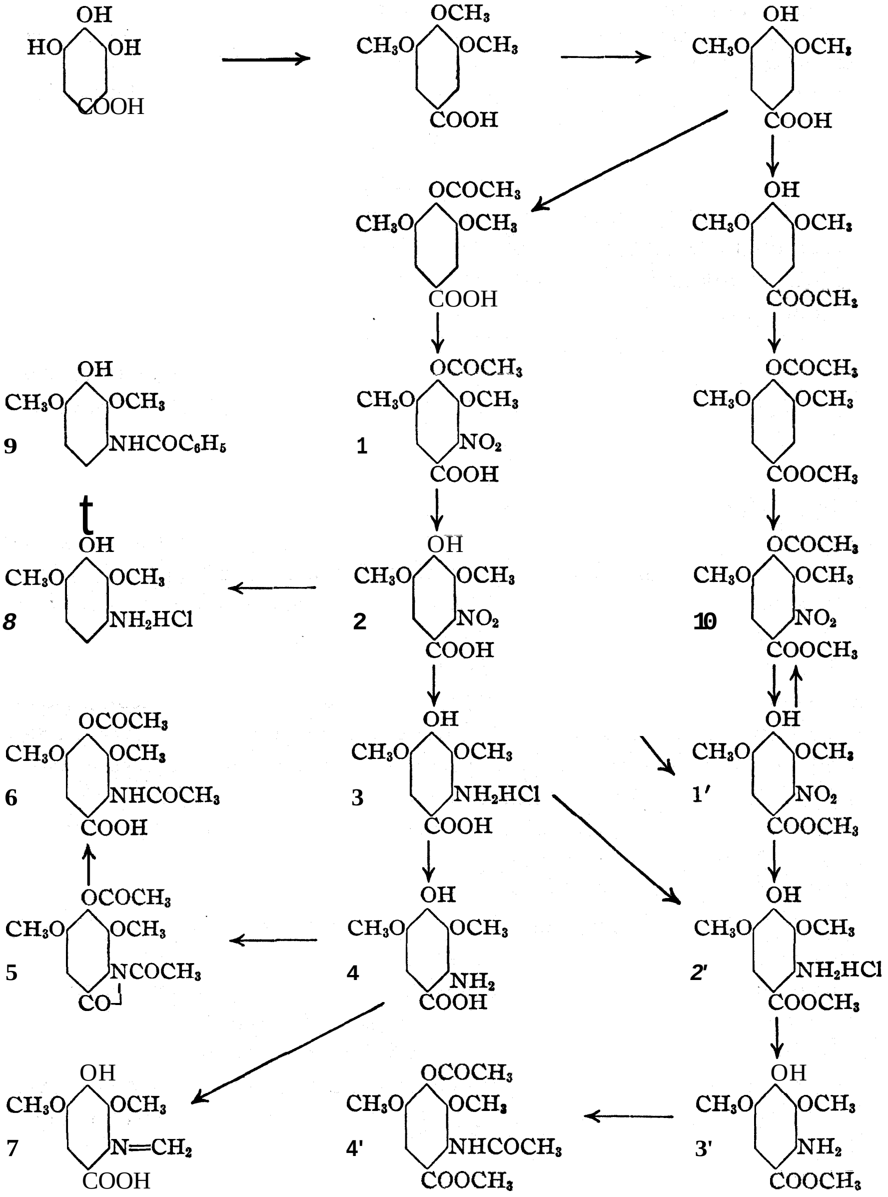
[2] DuPont Fellow at Columbia University, 1925–1927.

[3] (a) Bogert and Plaut, THIS JOURNAL, 37, 2723 (1915); (b) Bogert and Ehrlich, *ibid.*, 41, 798 (1919).

[4] (a) Harding, *J. Chem. Soc.*, 99, 1585 (1911); (b) De Lange, *Rec. trav. chim.*, 45, 19 (1926).

[5] (a) Hamburg, *Monatsh.*, 19, 598 (1898); (b) Power and Shedden, *J. Chem. Soc.*, 81, 73 (1902).

[6] Schiffer, *Ber.*, 25, 727 (1892).



The methylene-aminosyringic acid refused to yield the corresponding indigo, under the experimental conditions employed. This recalls the recent unsuccessful efforts of Overmyer[7] to prepare a hexamethoxy indigo from aminotrimethylgallic acid.

---

[7] Overmyer, THIS JOURNAL, 49, 499 (1927).

Experimental Part

Trimethylgallic Acid.—The method adopted for the preparation of this acid was based upon that of Graebe and Marta[8] as modified by Mauthner,[9] but involved a sufficient number of variations to make it seem advisable to describe the procedure.

A 5-liter flask containing 200 g. of gallic acid suspended in 1 liter of water was fitted with a 3-holed rubber stopper carrying thermometer, stopcock funnel tube and guard tube filled with sodium hyposulfite (to exclude oxygen). The acid was dissolved by the addition of a solution of 320 g. of sodium hydroxide and a small amount of sodium bisulfite (to prevent oxidation) in 1 liter of water, and 356 g. of methyl sulfate was then run in gradually and the flask shaken for twenty to thirty minutes while the temperature of the mixture was maintained below 35°. When evolution of heat was no longer caused by the reaction, a further 356 g. of methyl sulfate was added and the temperature of the mixture allowed to rise to 45°, after which it was refluxed for two hours, 80 g. of sodium hydroxide added (to saponify excess of methyl sulfate), the refluxing continued for a further two hours, the solution cooled, acidified with dilute hydrochloric acid, the precipitate collected, washed with cold water and recrystallized from a large volume of boiling water in the presence of a decolorizing carbon. The colorless crystalline product melted at 168" (corr.), in agreement with the literature; yield of crude product, 220 g., or 87%; after one crystallization, 180 g., or 72%, without figuring in that still recoverable from the mother liquor. It did not pay, however, to work over the mother liquor from the precipitation of the original crude acid,

As Overmyer[7] has pointed out, the crude product may be crystallized also from glacial acetic acid.

The use of sodium hydrosulfite, in place of the bisulfite, to prevent oxidation during the methylation of the gallic acid, was not so satisfactory and often imparted a foul odor to the product, possibly due to the formation of traces of mercaptan or sulfide from the methyl sulfate.

Syringic Acid.—Most of this acid required for the experimental work was obtained from the trimethylgallic acid by the method of Bogert and Ehrlich.[3b]

Alimchandani and Meldrum,[10] as well as others, have suggested the use of concentrated sulfuric acid, in place of the fuming acid, for accomplishing this demethylation but, in our experience, unless the reaction was conducted as follows, the product contained some unchanged trimethylgallic acid.

To 300 g. of concentrated sulfuric acid, 60 g. of trimethylgallic acid was added all at once and the solution kept for six hours at 40° with occasional agitation. It was allowed to cool, left overnight at room temperature and then stirred into 300 cc. of water without external cooling. The syringic acid which separated was collected, washed with cold water and crystallized from boiling water in the presence of a decolorizing carbon. From the original mother liquor more syringic acid separated on standing and

---

[8] Graebe and Martz, *Ann.*, 340,219 (1905).

[9] Mauthner, "Organic Syntheses," John Wiley and Sons, Inc., New York, *6*, 96 (1926).

[10] Alimchandani and Meldrum, *J. Chem. Soc.*, 117,967 (1920).

on concentration. Additional amounts may be recovered from the wash waters and second mother liquor; total yield of crude acid, **45** g., or **80%;** after one crystallization, **35** g., or **63%.** The carefully purified acid was odorless. The melting point varies somewhat depending upon the rapidity of heating and is generally preceded by a sintering or softening. The product obtained as described sintered at 204° and melted at **206.5**" (corr.). Koerner[11] and Gadamer[12] reported the m. p. as **202°,** Graebe and Martz[8] and Bogert and Ehrlich[3b] as **204°,** Alimchandani and Meldrum[10] as **206–207**" and Anderson and Nabenhauer[13] as **209–210".**

The methyl ester was obtained easily and in good yield by the method of Bogert and Ehrlich[3b] and in the anhydrous form melted at **107**" (corr.), as stated by them; yield, 75%.

Acetylsyringic acid was prepared first by Gadamer,[14] by the oxidation of acetylsinapinic acid, and more recently by Anderson and Nabenhauer,[13] by oxidation of the acetyl derivative of the anthocyanidin of Isabella grapes and by the direct acetylation of syringic acid. Our procedure differed somewhat from the latter. A suspension of **10** g. of syringic acid in **30** g. of acetic anhydride was warmed gently until a clear solution was obtained, **0.5** g. of fused sodium acetate was added and the solution left overnight at room temperature. The next morning the solution, including any crystals which had separated, was poured into **100** cc. of water and stirred thoroughly, to insure the hydrolysis of any excess anhydride. As the solution cooled, the crude acetylsyringic acid crystallized in amount essentially equal to that calculated. By a single recrystallization from water the pure acid was secured, m. p. 190.5° (corr.); yield, 78%, without including that recoverable by working over the mother liquors. Gadamer reported a m. p. of **181–183";** Anderson and Nabenhauer, **190–191°.**

When this acid was dissolved in absolute methanol and the solution saturated with dry hydrogen chloride, the acetyl group was removed and the carboxyl simultaneously esterified, with production of methyl syringate.

The methyl ester was prepared similarly, by direct acetylation of methyl syringate. as carried out first by Bogert and Plaut,[3a] and later by Alimchandani and Meldrum;[10] yield of crude product, 97%. Recrystallized from alcohol, the pure ester melted at **131.5**" (corr.). Bogert and Plaut found a m. p. of 129° (corr.) and Alimchandani and Meldrum reported **131°.**

Nitrosyringic Acid.—A suspension of **9** g. of nitro-acetylsyringic acid (see beyond) in **150** cc. of **5%** hydrochloric acid was refluxed until a clear solution was secured (about two hours). As the solution cooled, the nitrosyringic acid separated in long pale yellow needles, carrying one mole of water, some of which was lost even at room temperature; yield, 91%. Recrystallized from water, or from dilute (30%) alcohol, and dried at 110°, it formed colorless crystals which softened at 213° (corr.) and melted with decomposition at 218° (corr.); yield, 78%.

Anal. Calcd. for $C_9H_9O_7N$: C, **44.44;** H, **3.70.** Found: **C, 44.46;** H, **3.74.**

The product was soluble more or less freely in alcohol, ether, acetone or boiling water, but slightly soluble in cold water or in strong hydrochloric acid and practically insoluble in petroleum ether, chloroform or benzene. It dissolved in sodium bicarbonate solution, coloring it red. In contradistinction to the well-known sweet taste of o-nitrobenzoic acid, the taste of this analog was sour and brackish.

The introduction of this nitro group interfered so seriously with the methylation of the hydroxyl group in the meta position that such methylating agents as methyl

---

[11] Koerner, Gazz. *chim. ital.*, **18,215 (1888).**

[12] Gadamer, ***Ber.*****, 30,2330 (1897).**

[13] Anderson and Nabenhauer, THIS JOURNAL, **48,2997 (1926).**

[14] Gadamer, **Arch.** *Pharm.*, **235, 570 (1897).**

iodide and methyl sulfate were without effect upon it. This is in accord with the experience of Hemmelmayr,[15] who encountered similar difficulties in trying to methylate nitro-β-resorcylic acid.

Methyl Ester.—This was obtained by digesting methyl nitro-acetylsyringate with dilute hydrochloric acid, in practically the same way as just described for the free acid; yield of crude product, **95%.** Recrystallized from alcohol, it formed colorless needles, m. p. 210° (corr.); yield, **83%.**

Anal. Calcd. for $C_{10}H_{11}O_7N$: C, 46.69; H, 4.28. Pound: C, **47.05;** H, **4.50.**

The same product was obtained by dissolving nitrosyringic acid or its acetyl derivative in absolute methanol and saturating the solution with dry hydrogen chloride.

This nitro ester was very stable toward both acids and alkalies and could not be hydrolyzed to the free acid without decomposition. The experience of Schiffer[16] with ethyl nitrotriethylgallate, or of Thorns and Siebeling[17] with methyl nitrotrimethylgallate, was much the same.

Bogert and Plaut[3a] nitrated methyl syringate, in acetic anhydride solution, at low temperature, and reported the formation of a methyl nitrosyringate, melting at 68.3" (corr.), and that the same product was obtained by the action of concentrated (48%) hydrobromic acid upon methyl nitrotrimethylgallate, but we have been unable to check this direct nitration of methyl syringate or obtain the product, m. p. 68.3°, reported by them.

We endeavored to repeat this direct nitration of methyl syringate, but found the crude product very difficult to purify (as did Bogert and Plaut also), and failed to isolate either the compound of m. p. 68.3°, or the one of m. p. 210°. Further work is necessary to explain this discrepancy in results since, as noted beyond, both products seem to yield the same aminosyringate on reduction.

Nitro-acetylsyringic Acid, $(CH_3O)_2(CH_3COO)C_6H(NO_2)COOH$.—A mixture of 10 g. of acetylsyringic acid and **30** g. of acetic anhydride was nitrated with 5 cc. of fuming nitric acid (sp. gr. **1.6)** at −5°, adding the nitric acid very slowly with vigorous mechanical stirring. The acetylsyringic acid used must be pure and dry and the addition of the nitric acid be conducted very carefully, especially at first, or the reaction may proceed with explosive violence. After all of the nitric acid had been added, the stirring was continued for an hour longer, when a mass of minute crystals separated. After this mixture had stood for two hours at low temperature, it was poured into **200** cc. of **ice** water, the mixture well agitated to hydrolyze any excess of acetic anhydride and the insoluble nitro acid collected and orystallized from 50% alcohol. The product formed colorless, minute, diamond-shaped plates which melted with decomposition at **190"** (corr.). It dissolved in sodium bicarbonate solution to a colorless solution. but in aqueous sodium hydroxide a red color developed rapidly; yield of crude product, **92%;** of pure substance, **82%.** It dissolved quite readily in acetone or hot alcohol, less easily in ether or chloroform and was difficultly soluble or insoluble in water, petroleum ether or benzene.

A 1:1 mixture of acetylsyringic and nitro-acetylsyringic acids melted at 158–165°.

Anal. Calcd. for $C_{11}H_{11}O_8N$: C, **46.34;** H, 3.89. Found: C, **46.28;** H, **3.99.**

---

[15] Hemmelmayr, *Monatsh.,* **26, 185 (1905).**

[16] Schiffer, *Ber.,* **25, 727 (1892).**

[17] Thorns and Siebeling, *ibid.,* **44,** 2115 (1911).

The methyl ester was obtained by nitrating methyl acetylsyringate in the manner just described for the acid itself and also by the acetylation of methyl nitrosyringate with acetic anhydride and sodium acetate. The pure ester crystallized from **95%** alcohol in long, colorless needles, m. p. 107.5° (corr.); yield of crude product, 98%, of pure substance **85%.**

Anal. Calcd. for $C_{12}H_{13}O_8N$: C, **48.16;** H, **4.35.** Found: C, **48.09;** H, **4.38**

Aminosyringic Acid.—To a solution of 5 g. of stannous chloride in 10 cc. of concentrated hydrochloric acid, containing a little metallic tin, there was added gradually 5 g. of finely powdered nitrosyringic acid. During the addition of the nitro acid the mixture was stirred mechanically, its temperature was maintained at 40–45°, and tin and hydrochloric acid were replenished from time to time until a total of **10** g. of the former and **250** cc. of the latter had been used. The nitro acid slowly dissolved and the colorless tin double salt of the amino acid separated. Too much nitro acid should not be added at a time, since the separated tin double salt tends to coat it over and protect it from reduction. When the reduction was complete, the double salt was collected, washed with concentrated hydrochloric acid, dissolved in water and de-tinned by hydrogen sulfide. The filtrate from the stannous sulfide was evaporated under diminished pressure, at room temperature first and then at 60°. Colorless, fine needles of the amino acid hydrochloride were obtained, melting with decomposition at 185° (corr.); yield, 59%. It was partly hydrolyzed by pure water, but could be crystallized from dilute hvdrochloric acid.

It was dissolved in water, a slight excess of ammonium hydroxide solution and a little sodium sulfite (to retard oxidation) added, and then dilute acetic acid in slight excess. When the solution was cooled, the free amino acid separated in colorless needles which, after recrystallization from water, melted with decomposition at 169° (corr.); yield of crude acid, **97%;** of pure product, **86%.**

Anal. Calcd. for $C_9H_{11}O_5N$: C, 50.74; H, **5.16.** Found: C, **50.98;** H, **4.97.**

The troublesome tin sulfide precipitation may be avoided and the amino acid obtained more quickly, although in somewhat lower yield, by dissolving the tin double salt in a small amount of water, adding sufficient ammonium hydroxide solution to precipitate all of the tin as hydroxide, neutralizing the filtrate with acetic acid and recovering the amino acid as already described.

The free acid is moderately soluble in acetone, hot water or hot alcohol, only slightly soluble in ether or chloroform and practically insoluble in petroleum ether or benzene. Its hydrochloride was treated with potassium cyanate, for the purpose of getting the corresponding ureido acid, but the results were negative.

Methyl Ester.—Prepared by reduction of the methyl nitrosyringate with tin and hydrochloric acid, essentially as described by Bogert and Plaut,[3a] the hydrochloride was obtained in colorless needles which darkened at 192° and melted with decomposition at 217° (corr.); yield, **65%.** Bogert and Plaut gave the m. p. as 192°.

Anal. Calcd. for $C_{10}H_{14}O_5NCl$: Cl, **13.48.** Found: Cl, **13.80.**

A few crystals of sodium sulfite were added to an aqueous solution of this hydrochloride and the free ester was then precipitated by a slight excess of sodium bicarbonate and crystallized from dilute alcohol in the dark, as recommended by Bogert and Plaut. The colorless granular crystals obtained melted at 126.5° (corr.). Bogert and Plaut reported a m. p. of 110° (corr.).

The same product was secured by dissolving the aminosyringic acid in absolute methanol, saturating the cold solution with dry hydrogen chloride, dissolving the resultant hydrochloride in water and precipitating the solution by the addition of sodium bicarbonate.

Anal. Calcd. for $C_{10}H_{13}O_5N$: C, 52.86; H, 5.73. Found: C, 52.53; H, 5.59.

Attempts to hydrolyze this ester to the free acid all failed, acids or alkalies causing deeper-seated changes.

When this ester was diazotized and the diazo solution treated with cuprous oxide, a vigorous evolution of nitrogen occurred and the product isolated proved to be methyl syringate; yield, 69%. Power and Shedden[18] diazotized ethyl aminogallate and succeeded in isolating a diazo derivative, which lost nitrogen when heated with water at 220" and gave ethyl gallate.

Acetanthranil of Acetylsyringic Acid, $(CH_3O)_2(CH_3COO)C_6HN(COCH_3)CO$.—When a solution of aminosyringic acid (3 g.) in acetic anhydride (9 cc.), containing a trace of fused sodium acetate, was allowed to stand, crystals of this acetanthranil separated, which were recrystallized from acetic anhydride or from dry benzene. The compound then formed colorless needles, m. p. 169" (corr.); yield, 78%.

Anal. Calcd. for $C_{13}H_{13}O_6N$: C, 55.91; H, 4.66. Found: C, 55.82; H, 4.71.

The conversion of this acetanthranil into quinazolones, by the action of amines,[19,20] has not been accomplished as yet. Preliminary experiments with ammonia and aniline seem to indicate that it is less reactive in this respect than acetanthranil itself.

Acetamino-acetylsyringic acid, $(CH_3O)_2(CH_3COO)C_6H(NHCOCH_3)COOH$, was obtained very easily from the above acetanthranil by evaporating its aqueous solution, and was recrystallized from water; m. p. 193° (corr.); yield, 75%.

Anal. Calcd. for $C_{13}H_{15}O_7N$: C, 52.52; H, 5.05. Found: C, 52.23; H, 4.98.

Methyl Ester.—Prepared as described by Bogert and Plaut.[3a] The colorless crystals secured by us melted at 154° (corr.), whereas Bogert and Plaut found a m. p. of 139.9" (corr.).

Anal. Calcd. for $C_{14}H_{17}O_7N$: C, 54.02; H, 5.47. Found: C, 53.91; H, 5.44.

Structurally this acid is of methacetin type but no pharmacological tests have been conducted with it.

Hydrochloride of **3-Amino-2,6-dimethylpyrogallol,** $(CH_3O)_2(HO)C_6H_2NH_2$.—A suspension of 10 g. of nitrosyringic acid in 100 cc. of concentrated hydrochloric acid was heated under a reflux condenser, while 20 g. of tin was added gradually. When solution was complete (about four to five hours), the mixture was cooled, the double tin salt collected, dissolved in water, the tin precipitated as sulfide, the filtrate evaporated to dryness under diminished pressure and the residue crystallized from water. Large. colorless orthorhombic crystals of the hydrochloride resulted, m. p. 198° (corr.) with decomposition; yield, 78%.

Anal. Calcd. for $C_8H_{12}O_3NCl$: Cl, 17.27. Found: Cl, 17.24.

When nitrosyringic acid was boiled with ferrous sulfate and ammonium hydroxide solution, the aminopyrogallol dimethyl ether was again the product.

Benzoyl Derivative.—This was prepared by the action of benzoyl chloride upon the amine, in the presence of a slight excess of sodium bicarbonate and a few crystals of sodium sulfite. It crystallized from alcohol in large colorless flakes, m. p. 158.3° (corr.); yield, almost that calculated.

Anal. Calcd. for $C_{15}H_{15}O_4N$: C, 65.93; H, 5.50. Found: C, 66.06; H, 5.56.

Its alcoholic solution was colored deep red by ferric chloride. It was insoluble in cold dilute hydrochloric acid, or in sodium bicarbonate solution.

---

[18] Power and Shedden, J. *Chem. Soc.*, **81,** 73 (1902).

[19] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35,3480 (1902).

[20] Bogert and Chambers, THIS JOURNAL, 27,649 (1905).

Methylene-aminosyringic Acid, $(CH_3O)_2(OH)C_6H(N{=}CH_2)COOH$.—A solution of aminosyringic acid (1 g.) in dilute hydrochloric acid (2 cc. of acid: 10 cc. of water) was cooled to 0° and a 40% formaldehyde solution (3 cc.) added slowly. The colorless crystals which separated were removed, dried and recrystallized from a mixture of chloroform and carbon tetrachloride, when they softened at 191° (corr.), and melted with decomposition at 195° (corr.); yield, 75%. When it was warmed with dilute sulfuric acid, formaldehyde was evolved.

Anal. Calcd. for $C_{10}H_{11}O_5N$: C, 53.33; H, 4.88. Pound: C, 53.40; H, 4.79.

The crystals of methylene-anthranilic acid are luminescent in the dark when rubbed,[21] but these crystals were not.

Experiments conducted for the purpose of converting this methylene derivative into the corresponding glycine nitrile and indigo have proved unsuccessful so far.

Summary

1. The preparation and properties of the following new compounds are described: nitrosyringic acid, nitro-acetylsyringic acid and its methyl ester, aminosyringic acid, its hydrochloride, acetanthranil, diacetyl and methylene derivatives, 3-aminopyrogallol-2,6-dimethyl ether, its hydrochloride and benzoyl derivative.

2. In the case of methyl nitrosyringate, methyl aminosyringate, the hydrochloride and diacetyl derivative of the latter, the melting points found differ from those already in the literature.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OR PRINCETON UNIVERSITY]

SOME OBSERVATIONS ON THE CATALYTIC ACTIVITY OF ALUMINUM CHLORIDE

BY GREGG DOUGHERTY

RECEIVED OCTOBER 13, 1928 PUBLISHED FEBRUARY 5, 1929

Aluminum chloride forms addition compounds with many different types of organic molecules, and in almost every attempt to explain the mechanism of the Friedel-Crafts reaction, the catalytic activity of the aluminum chloride has been connected with the formation of these complexes. Little is known concerning the nature of the addition compounds and no adequate reasons for their catalytic activity have been suggested.

The additive power of aluminum chloride is usually explained electronically on the ground that the aluminum atom in aluminum chloride possesses an outer shell of six electrons, and in order to achieve the more stable arrangement of eight, it will share a pair previously belonging totally to some other atom or molecule. Unless a rearrangement of some sort occurs, this new molecule, according to the ideas of Lowry[1] and Sidg-

---

[21] Badische Anilin- und Soda Fabrik, German Patent 158,090; *Friedländer,* 8, 397 **(1905).**

[1] Lowry, J. *Chem. Soc.,* 123,822 (1923); *Phil. Mag.,* 45,964,1013 (1923).

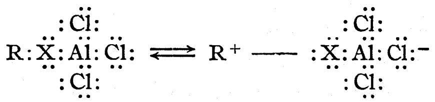
wick,[2] should have a polar character. It would seem likely that the active agents in the Friedel-Crafts synthesis are these polarized or even ionized addition compounds which exist, possibly in very small amount only, in equilibrium with the undissociated or unpolarized molecules. It is a fact that solutions of aluminum halides in alkyl halides, and organic aluminum halide solutions in general, often show considerable conductivity.

An explanation of the mechanism of the Friedel-Crafts synthesis involving in part this idea was advanced by the present author and published as an insert in an article on synthetic anthraquinone by K. H. Klipstein.[3]

Lately H. J. Prins[4] has suggested that under the influence of aluminum chloride benzene polarizes or ionizes in such a way as to give effectively a hydrogen ion and a phenyl ion. In this paper the ideas mentioned above concerning the nature of the Friedel-Crafts reactions are extended and the results of some experimental work bearing on the problem are offered.

Theoretical Part

If one adopts the current ideas of the electronic theory of valence, it is possible to show that if aluminum chloride adds to benzene and there is a subsequent polarization or dissociation, the probable result would be a polarized molecule of the type $(C_6H_5AlCl_3)^-$—H^+ or the ions $(C_6H_5AlCl)^-$ and H^+. Similarly, with an alkyl halide, RX, we would obtain



$$R:\underset{..}{\overset{..}{X}}:\underset{:\underset{..}{Cl}:}{\overset{:\overset{..}{Cl}:}{\underset{..}{\overset{..}{Al}}}}:\underset{..}{\overset{..}{Cl}}: \rightleftharpoons R^+ \text{——} :\underset{..}{\overset{..}{X}}:\underset{:\underset{..}{Cl}:}{\overset{:\overset{..}{Cl}:}{\underset{..}{\overset{..}{Al}}}}:\underset{..}{\overset{..}{Cl}}:^-$$

or R^+ and $(X\ Al\ Cl_3)^-$. The simplest example of the Friedel-Crafts reaction in which the action is truly catalytic, that is, the aluminum chloride is not taken from the system as the process proceeds in the form of a very inert addition compound with one of the resultants, as in a ketone synthesis, would be represented by the following

$$C_6H_6 + AlCl_3 \rightleftharpoons C_6H_6AlCl_3 \rightleftharpoons (C_6H_5AlCl_3)^-\text{—}H^+ \qquad (1)$$

$$RX + AlCl_3 \rightleftharpoons RXAlCl_3 \rightleftharpoons R^+\text{—}(XAlCl_3)^- \qquad (2)$$

$$(C_6H_5AlCl_3)^-\text{—}H^+ + R^+\text{—}(XAlCl_3)^- \rightleftharpoons (C_6H_5AlCl_3)^-\text{—}R^+ + H^+\text{—}(XAlCl_3)^- \qquad (3)$$

$$(C_6H_5AlCl_3)^-\text{—}R^+ \rightleftharpoons C_6H_5R\cdot AlCl_3 \rightleftharpoons C_6H_5R + AlCl_3 \qquad (4)$$

$$H^+\text{—}(XAlCl_3)^- \rightleftharpoons HX\cdot AlCl_3 \rightleftharpoons HX + AlCl_3 \qquad (5)$$

These reactions indicate a situation somewhat similar to that which we have presumably when inorganic ionogens react. There would be displacement in one direction or another if any pair of ions formed an insoluble compound or a very volatile one. In the above a nearly complete reaction results due to the volatility of the hydrogen chloride. As the

---

[2] Sidgwick, "The Electronic Theory of Valency," Oxford, 1927, Chapter IV.

[3] Klipstein, *Ind. Eng. Chem.*, 18, 1327 (1926).

[4] Prins, *Chem. Weekblud,* 24,615 (1927).

reactions indicate, the reaction should be reversible and it is a fact that we can de-alkylate alkyl benzenes by means of aluminum chloride and a stream of hydrogen chloride. In actual practice the situation is not so simple as the equations would lead one to believe. This is due to the fact that the C_6H_5R can add to aluminum chloride and become part of a polarized or ionized molecule just as benzene does. The result is a reaction mixture containing various polyalkylated benzenes in addition to the mono-alkyl compound. The former are formed in a proportion depending on the relative tendency to add to aluminum chloride and the extent to which each of the resulting addition compounds is dissociated.

The Action of Aluminum Chloride on Halogen Compounds.—The reactions given above for the formation of alkylbenzenes suggest that if benzene were replaced by another alkyl halide, or a halogen compound of like properties, different from RX, metathetical reactions should occur essentially similar in type to those of Friedel and Crafts. Such reactions would be represented by the following

$$RX + AlCl_3 \rightleftharpoons RX\cdot AlCl_3 \rightleftharpoons R^+\text{—}(XAlCl_3)^- \qquad (6)$$

$$R_1X_1 + AlCl_3 \rightleftharpoons R_1X_1\cdot AlCl_3 \rightleftharpoons R_1{}^+\text{—}(X_1AlCl_3)^- \qquad (7)$$

$$R^+\text{—}(XAlCl_3)^- + R_1{}^+\text{—}(X_1AlCl_3)^- \rightleftharpoons R^+\text{—}(X_1AlCl_3)^- + R_1{}^+\text{—}(XAlCl_3)^- \qquad (8)$$

$$R^+\text{—}(X_1AlCl_3)^- \rightleftharpoons RX_1 + AlCl_3, \text{ and } R_1{}^+\text{—}(XAlCl_3)^- \rightleftharpoons R_1X + AlCl_3 \qquad (9)$$

If either of the new alkyl halides, R_1X or RX_1, happened to be volatile in comparison with RX and R_1X_1, the reaction $RX + R_1X_1 \longrightarrow R_1X + RX_1$ should occur. On the other hand, if all of the alkyl halides were of the same order of volatility, the reaction should proceed to an equilibrium point.

There are many cases noted in the literature in which there is an exchange of halogen between metallic halides and aliphatic halogen compounds,[5] but the only example found in which there was actual transfer from one hydrocarbon radical to another under the influence of aluminum chloride was one in which an alkyl iodide was involved. Walker[6] observed that when a small amount of aluminum chloride was added to a mixture of ethyl iodide and chloroform, a vigorous reaction resulted; the products were ethyl chloride and iodoform. Similarly, methyl iodide and carbon tetrachloride yielded methyl chloride and carbon tetra-iodide. He seemed doubtful whether these transformations were general and would take place in the case of mixtures of chlorides and bromides.

In order to make sure that Walker's reactions involving iodides were general and not specific to mixtures containing chloroform or carbon tetrachloride, some experiments have been carried out in which the chlorides were replaced by bromides. Methyl iodide and ethyl bromide were mixed and a small piece of aluminum chloride was added. After gentle warming for a minute, a vigorous reaction commenced; methyl bromide

---

[5] Meyer, J. *prakt. Chem.*, [2] **34**, 104 (1886); Pouret, *Compt. rend.*, **130**, 1191 (1900); Ber., [3] 25, 191, 293 (1901).

[6] Walker, *J. Chem. Soc.*, *85*, 1082 (1904).

was evolved and ethyl iodide was isolated. Twenty g. of ethylene bromide and 30 g. of ethyl iodide were mixed and 1 g, of aluminum chloride was added. Here again there was a vigorous reaction; ethyl bromide was evolved and obtained in about a 70% yield. Undoubtedly the principal reactions which occurred were as follows

$$CH_3I + C_2H_5Br \longrightarrow CH_3Br\uparrow + C_2H_5I$$
$$C_2H_4Br_2 + C_2H_5I \longrightarrow C_2H_5Br\uparrow + C_2H_4I_2$$

The reaction mixtures became highly colored as soon as the aluminum chloride was added, some free iodine was liberated, tars were formed and the reactions were not clean cut.

Since alkyl iodides cannot be used successfully in the Friedel-Crafts syntheses, a reaction between chlorides and bromides in the presence of aluminum chloride would have much more bearing on the point under discussion. Walker observed that if chlorides and bromides react at all, they do so very slowly. It has been found that they do react and, under the proper conditions, without appreciable formation of complex by-products and tars. A solution was made of one mole of ethyl bromide and one of chloroform and a small amount of aluminum chloride added. There was distinct warming and the appearance of a bright red color. When warmed to 45–50°, there was bubbling and a slow evolution of ethyl chloride but no such activity as in the case of the iodides. Some hydrogen halide was formed and raising the temperature increased the amount, so it seemed best not to attempt to distil out all of the ethyl chloride formed in this way but to allow the reaction mixture to stand at room temperature. After thirty-six hours, water and dilute hydrochloric acid were added, the liquid was washed with dilute sodium hydroxide solution and dried over calcium chloride. On fractionating, in addition to a very low boiling portion which represented the remainder of the ethyl chloride formed, an ethyl bromide and a chloroform fraction, there was a small amount of liquid (b. p. 120–122°) and a rather larger fraction (b. p. 88–93'). The latter on redistillation boiled constantly at 91–92' and had a specific gravity of 1.975 at 15°. These are the properties of dichloromonobromomethane. *Anal.* Calcd. for $CHBrCl_2$: Cl and Br, 92.06. Found: 91.80. In this and other experiments the yield of the mixed halogen compound was about 35% of the theoretical based on the equation: $CHCl_3 + C_2H_5Br \longrightarrow CHCl_2Br + C_2H_5Cl$. The small fraction (b. p. 120–132") ran high in halogen, above 93%, and was probably a mixture of dibromomonochloromethane and bromoform. Difficulties in the fractional distillation made it impossible to identify these two compounds with certainty or to make anything like a quantitative separation of all the constituents in the reaction mixture. Both tar formation and the evolution of hydrogen halide seemed to increase with rise of temperature and were kept at a minimum by running the reaction at 20–25°.

In order to make a semi-quantitative study of this type of reaction and to test its reversibility, reactants were chosen which should produce only one new compound and that one not very volatile. Ethylene bromide and ethylene chloride should give ethylene chlorobromide: $C_2H_4Cl_2 + C_2H_4Br_2 \longrightarrow 2C_2H_4ClBr$. The reactants were mixed in equimolar proportions and about 0.04 of a mole of aluminum chloride added. It was found that the reaction was complete after standing for 35 hours at 25°. The reaction mixture was treated as in the case of the chloroform–ethyl bromide experiment and submitted to careful and repeated fractional distillation using an efficient fractionating column. Only three distinct fractions were found: the first and third had the properties of the reactants, while the middle one (b. p. 106–109") had a specific gravity of 1.73 at 19°, agreeing with that of ethylene chlorobromide. A halogen determination gave 80.7%; calculated for C_2H_4ClBr, 80.45%. Careful weighing of the fractions and taking account of losses of manipulation and material left in the fractionating apparatus indicated that the above reaction was complete when the three compounds were present in the ratio of 2 moles of ethylene chlorobromide to one each of ethylene chloride and ethylene bromide. This is what might be expected on the law of chances if it is assumed that the system contains highly polarized or ionized molecules and the energy content of the three compounds is approximately the same.

An attempt was made to test the reversibility of the reaction and to arrive at the equilibrium point from the other direction. Ethylene chlorobromide and aluminum chloride were mixed and allowed to stand under the same conditions as in the previous experiment. On fractionating the same three fractions were obtained and the weights were approximately in the same ratio, which indicates that the reaction is easily reversible and should be represented by the equation: $2C_2H_4ClBr \rightleftharpoons C_2H_4Cl_2 + C_2H_4Br_2$. The reaction mixtures darken in color as the reaction progresses and a small amount of hydrogen halide is evolved. Very little tar is formed, however, and this by-reaction is evidently very superficial in nature when the experiment is conducted at room temperature. To make sure that no exchange of halogen occurred between aluminum chloride and ethylene bromide, an experiment was tried in which ethylene chloride was omitted. The ethylene bromide was unchanged. Plans are being made to study these reactions more accurately; both equilibrium and velocity measurements will be attempted.

I wish to take this opportunity to thank Professor Frank O. Rice of Johns Hopkins University for his helpful advice in carrying out this work, and the Department of Chemistry at Johns Hopkins University for so kindly allowing me the privileges of the laboratory during the spring term of 1927–1928.

Summary

A mechanism for the Friedel-Crafts reaction has been suggested.

The hypothesis predicts that metathetical reactions will occur between certain types of aliphatic halogen compounds in the presence of aluminum chloride. Experimental evidence is given that such reactions do occur, and some of them have been studied.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF EPHEDRINE AND STRUCTURALLY SIMILAR COMPOUNDS. I. A NEW SYNTHESIS OF EPHEDRINE

BY RICHARD H. F. MANSKE[1] AND TREAT B. JOHNSON

RECEIVED OCTOBER 15, 1928 PUBLISHED FEBRUARY 5, 1929

Although the constitution of ephedrine (III) is no longer in doubt, interest in this base has been renewed by the pharmacological work of K. K. Chen.[2] Since it seemed not improbable that other bases analogously constituted might possess more desirable or at least interesting physiological properties,[3] the authors entered this field with a view to the improvement of known methods of synthesis or to the discovery of new ones.

---

[1] Holder of the Eli Lilly Company Research Fellowship in Organic Chemistry, 1927–1928.

[2] Chen and Kao, *J. Am. Pharm. Assocn.*, **8**, 625a (1926). Bibliography is given in this paper.

[3] Hyde, Browning and Adams, THIS JOURNAL, 50,2297 (1928).

It was observed that a solution of 1-phenyl-1,2-propanedione,[4] C_6H_5-$COCOCH_3$, in petroleum ether reacts exothermally with dried gaseous methylamine to form a colorless crystalline compound with the elimination of water. This substance is unstable and gradually decomposes to an indefinite mixture, Treatment with acids regenerates the two components and titration shows that approximately one molecule of amine is combined with one of the diketone. Aside from purely speculative formulas for this compound only two (I and II) need be mentioned, and of these the former may at once be disposed of on purely theoretical grounds.

$C_6H_5C{=}(NCH_3)COCH_3$	$C_6H_5COC{=}(NCH_3)CH_3$	$C_6H_5CH(OH)CH(NCH_3)CH_3$
I	II	III

The considerable affinity demand of the phenyl group[5] leaves the a-carbon relatively saturated so that any negative ions (CN, HSO_3, etc.) have a tendency to attach themselves to the β-carbon in preference. Furthermore the effect of the carbonyl groups is reciprocal (the ketone group of ethyl pyruvate is more reactive than those of acetone, ethyl acetoacetate, or ethyl levulinate),[6,7] that is, each enhances the additive capacity of the other. Finally, methylbenzyl ketone reacts readily with bisulfites, whereas ethylbenzyl ketone does not, and the former is more reactive than acetone,' so that the phenyl group enhances the additive capacity of the β-carbon, an effect in accord with the Flürscheim's theory of alternate affinity demand.[5]

Sufficient experimental proof of the correctness of Formula (II) is found in the fact that catalytic reduction leads to ephedrine (111), that is, the carbonyl group is reduced to a secondary alcohol and the imino double bond (—C=N—) is reduced at the same time.

It is interesting to note that only a very small proportion of \$-ephedrine accompanies the main product, dl-ephedrine. The method of Eberhardt[S] yields a considerable amount of the ψ-form and that of Spath and Gohring[S] yielded the \$-form almost exclusively. To offer an explanation for this observation the authors assume that there is a repulsion between the N- and the ketonic O-atoms, their mean positions in space being on opposite sides of the carbon chain, so that the reduced product also tends to have the HO- and CH_3NH-groups distant from each other, a postulate already

---

[4] This diketone was prepared by the action of NO_2 on propiophenone. The details will form the subject of a future communication. See also a paper by Gilman and Johnson, THIS JOURNAL, 50,3341 (1928).

[5] Fliirscheim, J. *Chem. Soc.*, 95,718 (1909); 97, 87 (1910).

[6] Lapworth, *ibid.*, 83,997 (1903).

[7] The result of a systematic investigation carried out at the University of Manchester in England and to be published shortly in the *Journal of the Chemical Society*, first paper, Lapworth and Manske, J. *Chem. Soc.*, 1928,2533.

[8] Eberhardt, *Arch. Pharm.*, 258, 97 (1920).

[9] Späth and Gohring, *Monatsh.*, 41,319 (1920).

advanced on other grounds for ephedrine. Conversely, it has been proposed that these groups are specially adjacent in ψ-ephedrine.[10]

Experimental Part

&Ephedrine.—A mixture of 50 cc. of absolute ethyl alcohol, 7.4 g. of methylphenyl diketone ($^1/_{20}$ mole) and an alcoholic solution of methylamine containing 1.6 g. ($^1/_{20}$ mole) was reduced catalytically with hydrogen in the presence of 0.1 g. of platinum oxide.[11] In some experiments there was a long induction period and then the yield was low. This behavior could be obviated by reducing the catalyst first and then adding the reactants. When reduction no longer proceeded, the catalyst was removed by filtration and about half the alcohol removed under reduced pressure. By this means any excess of methylamine was removed. The solution was made just acid with alcoholic hydrogen chloride and evaporated to dryness. The solid hydrochloride was washed with cold acetone and dried. The yield was 2.5–4.0 g. A small amount of ψ-ephedrine hydrochloride could be extracted from this by means of hot chloroform and by working up a number of extractions sufficient was obtained for deiinite identification (m. p. 164°; free base, m. p. 118°).[9,11] The dl-ephedrine hydrochloride was purified by recrystallizing once from alcohol–acetone and melted at 189°.[9]

Anal. Calcd. for $C_{10}H_{15}ON\cdot HCl$: N, 6.95; Cl, 17.60. Found: N, 6.98; Cl, 17.70.

The free base was recrystallized from chloroform–petroleum ether and melted at 75°.[12]

Anal. Calcd. for $C_{10}H_{15}ON$: C, 72.71; H, 9.09; N, 8.49. Pound: C, 72.43; H, 9.01; N, 8.20.

Summary

1. A new reaction has been discovered whereby it is possible to synthesize the alkaloid ephedrine.
2. This reaction consists in taking advantage of the differential additive capacity of the two ketonic groups in alkylaryl o-diketones.
3. 1-Phenyl-1,2-propanedione condenses with one molecule of methylamine and the condensation product on reduction yields dl-ephedrine.
4. Several homologs of ephedrine have been synthesized by this method and their description will form the subject of an early communication.

NEW HAVEN, CONNECTICUT

---

[10] Henry, "The Plant Alkaloids," Blakiston Sons, 1924.

[11] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[12] Melting points are corrected.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

STUDIES IN THE DIPHENIC ACID SERIES. III

BY H. W. UNDERWOOD, JR., AND L. A. CLOUGH[1]

RECEIVED OCTOBER 17, 1928 PUBLISHED FEBRUARY 5, 1929

When the dichloride, diamide, diethyl ester, dimethyl ester, mono-ethyl ester, monomethyl ester, mono-amide and imide of diphenic acid are heated with concentrated sulfuric acid, each compound is transformed into a member of the diphenyleneketone-4-carboxylic acid series; evidently sulfuric acid causes a rotation of the rings in the biphenyl nucleus.[2] By means of acetic anhydride diphenic acid can be transformed into its anhydride and diphenimide secured from the mono-amide of diphenic acid;[2] these reactions are dehydrations and involve a joining of the side-chains attached to the rings. A part of this paper deals with an investigation of the action of acetic anhydride on the four esters of diphenic acid mentioned above, as well as the diamide; diphenamic acid has also been studied again.

p,p'-Dinitrodiphenic acid is unique in that it does not form an anhydride or a ketone acid; a plausible explanation of the behavior of this compound may be found by postulating that the meta orienting nitro group in each ring loosens the hydroxyl groups in the carboxyl and strengthens the bond which holds the hydrogen atom in the latter as well as the force holding the ring hydrogen which is meta to the nitro group. This idea would lead one to expect that a compound, such as *p,p'*-dibromodiphenic acid, in which the substituents are not meta orienting would form an anhydride. We have secured evidence regarding this point.

In a previous paper[3] it was pointed out that the results obtained by Bischoff and Adkins[4] regarding the condensation of diphenic anhydride and resorcinol were somewhat different from those which one of us described. Later Adkins, Steinbring and Pickering[6] questioned the validity of the criticisms. We are now ready to reaffirm the latter and to describe additional experimental evidence which supports our point of view.

Discussion of Experiments and Interpretation of Results

All of the temperatures given below are uncorrected.

Esters of Diphenic Acid.—The preparation of the monomethyl, mono-ethyl, dimethyl and diethyl esters of diphenic acid has been previously described.[2] Six g. of

---

[1] Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by L. A. Clough in partial fulfilment of the requirements for the degree of Master of Science.

[2] Underwood and Kochmann, THIS JOURNAL, 46, 2069 (1924).

[3] Underwood and Kochmann, *ibid.*, 45, 3071 (1923).

[4] Bischoff and Adkins, *ibid.*, 45, 1030 (1923).

[5] **Adkins,** Steinbring and Pickering, *ibid.*, 46, 1917 (1924).

each of these compounds was heated with 12 g. of glacial acetic acid and 18 g. of acetic anhydride for sixteen hours at 145°. The major part of the liquid was then removed by distillation and the residue kept in an ice chest until crystallization took place. In every case practically all of the ester was recovered unchanged. The results of these experiments indicate that the hydroxyl and alkoxyl groups in these esters are very firmly held.

Diphenamic Acid.—A mixture of 30 g. of diphenamic acid (the mono-amide of diphenic acid), 60 g. of glacial acetic acid and 60 g. of acetic anhydride was heated at 145° for one hour. The solid which formed upon cooling was collected on a filter, thoroughly washed with cold sodium carbonate solution and water and subsequently dried at 110°. This product, m. p. 219°, was identified as diphenimide. Acidification of the sodium carbonate extract yielded a precipitate which melted at 168° after washing with water and drying at 110°. The compound gave a qualitative test for nitrogen; heating with concd. ammonium hydroxide did not produce the diamide of diphenic acid and the melting point was not changed by recrystallization from ethyl alcohol and from water. It was thought that this substance might be 1-cyanobiphenyl-10-carboxylic acid. In order to check our hypothesis, analyses and hydrolyses were carried out. Approximately 0.5 g. of the compound melting at 168° was heated on a water-bath for four hours with a mixture of 2 cc. of 95% sulfuric acid and 3 cc. of water; the solid gradually dissolved. The cold reaction liquid was poured into water and the precipitate collected on a filter, washed with water and finally crystallized from ethyl alcohol. By means of a mixed melting point the product of the hydrolysis was identified as diphenic acid. Upon dilution of the acetic acidanhydride reaction mixture with water, more of the dissolved material was obtained; this was separated into its components by the procedure already described. The total yield of diphenimide was 18.2 g. and that of cyanobiphenylcarboxylic acid was 3.8 g.

Anal. Calcd. for $C_{14}H_9O_2N$: C, 75.31; H, 4.06; N, 6.28. Found: C, 74.70, 74.68; H, 4.35, 4.40; N, 6.60, 6.40.

Diamide of Diphenic Acid.—The solution obtained upon heating 10 g. of the diamide of diphenic acid, 25 g. of glacial acetic acid and 40 g. of acetic anhydride at 145° for eight hours was concentrated by distilling most of the liquid. When water was added to the residue a precipitate was formed. This was collected on a filter and dried at 110°. The solid, which was insoluble in cold sodium carbonate solution, did not melt sharply. By extraction with a large amount of hot methyl alcohol most of the product was dissolved. After about one-half of the solvent had been removed by distillation, the solution on standing deposited long, flat needles which melted at 172° when dry. Further concentration of the solution yielded a crystalline mass which apparently contained an impure acetyl derivative of the diamide; this material did not melt sharply. By careful treatment of the substance with dilute sodium hydroxide solution and subsequent recrystallizations from methyl alcohol, more of the compound melting at 172' was secured.

It was thought that the latter was 2,2'-dicyanobiphenyl produced by the removal of two molecules of water from one molecule of diphenic acid diamide. The compound was insoluble in solutions of sodium carbonate and sodium hydroxide; recrystallization from ether and from acetone did not change the melting point; qualitative tests showed the presence of nitrogen. Approximately 1 g. of the substance was heated on a water-bath for four hours with a mixture of 4 cc. of 95% sulfuric acid and 4 cc. of water; the solid gradually dissolved. The cold reaction liquid was poured into water, the precipitate collected on a filter, washed with water and finally crystallized from ethyl alcohol. By means of a mixed melting point the hydrolysis product was identified as diphenic acid. The use of more concentrated sulfuric acid and a shorter time of heating gave some diphenamic acid. These experiments as well as the neutral character of the substance and the results of analyses indicated that the compound melting at 172° was 2,2′-dicyanobiphenyl. In one run 1.9 g. of the latter was obtained from 10 g. of the diamide; it was difficult to get check yields on account of the necessity for several crystallizations. A small amount of the so-called acetyl derivative of diphenic acid diamide was purified by several crystallizations from large amounts of ether; the material melted sharply at 166–167°. It was not studied further since the isolation of it involved many troublesome steps and the compound did not appear to be important in our work. Treatment of the substance with dilute sodium hydroxide solution gave the diamide of diphenic acid.

Anal. (Crystals, m. p. 172°.) Calcd. for $C_{14}H_8N_2$: C, 82.32; H, 3.95; N, 13.72. Found: C, 81.80, 81.85; H, 4.17, 4.06; N, 14.05, 14.10.

***p,p′*-Dibromodiphenic Acid.**—Schmidt and Junghans[6] made *p,p′*-dibromodiphenic acid by the oxidation of 2,7-dibromophenanthraquinone. The procedure which we used was based upon their work; details are similar to those given by one of us in describing the preparation of *p,p′*-dinitrodiphenic acid,[2] except that glacial acetic acid was employed as a solvent. The oxidation proceeded very slowly and it was frequently necessary to remove the dibromodiphenic acid by treatment of the solid reaction product with sodium carbonate solution. Unchanged dibromophenanthraquinone was then heated with more oxidizing agent. This process was repeated several times. It was not possible to estimate yields accurately. The 2,7-dibromophenanthraquinone used in this experiment was prepared by another investigator; details of the procedure employed in making it are not available.

Approximately 1 g. of *p,p′*-dibromodiphenic acid (m. p. 277–278°), 10 g. of glacial acetic acid (solvent) and 20 g. of acetic anhydride were heated at 145° for eleven hours. After some of the liquid had been distilled, the reaction mixture upon cooling deposited crystals; these were collected on a filter, washed and dried. The white solid melted at 304–305°. It was insoluble in sodium carbonate solution; when heated with 20% aqueous sodium hydroxide it slowly dissolved; acidification of the liquid yielded *p,p′*-dibromodiphenic acid.

Anal. Calcd. for $C_{14}H_6O_3Br_2$: Br, 41.84. Found: Br, 41.50, 41.61.

This experiment shows that *p,p′*-dibromodiphenic acid readily forms an anhydride; the results support the ideas stated in the introductory part of the paper. However, it is necessary to consider the possibilities regarding stereoisomerism as well as the influence of ring substituents upon carboxyl groups in order to get a complete account of the reasons for the unique behavior of *p,p′*-dinitrodiphenic acid.

Condensation of Diphenic Anhydride with Resorcinol. Work of Bischoff and Adkins.—In commenting upon the investigation[3] by one of us, Adkins and his associates[5] declared (without stating detailed experimental evidence) that the use of a temperature (175°) higher than 135–150° for condensing diphenic anhydride and resorcinol caused fundamental changes in structure which were avoided by Bischoff and Adkins. It was also said that Bischoff early in his work learned that when the anhydride was condensed with resorcinol at temperatures in the vicinity of 175°, a non-fluorescent compound was formed, sometimes with the evolution of carbon dioxide. We believe this observation has an important bearing on the results which Bischoff and Adkins reported and that they should have mentioned it.

---

[6] Schmidt and Junghans, Ber., 37,3567 (1904).

In order to answer the question regarding the influence of temperature on this reaction, we carried out the experiment described by Bischoff and Adkins, using the proportions of reagents, temperature, time of heating and extraction procedure which they gave. We readily obtained crystals by dissolving the reaction product in alcohol and gradually diluting the solution with water. The carefully purified crystalline material (resorcinoldiphenein) dissolved in aqueous sodium hydroxide, forming a greenish-yellow liquid, but did not produce marked fluorescence. On the other hand, the amorphous residue (ketone acid derivative) gave a strongly fluorescent liquid when added to sodium hydroxide solution. We repeated the condensation three times; in every case the results were practically the same. By the use of a very small amount of the crystalline substance a melting point of 178–179° was found; these figures were previously given by one[3] of us. A mixture of the crystals obtained by the Bischoff and Adkins method and those prepared some time ago in this Laboratory melted at 247–249°. We also found that the melting point of our resorcinoldiphenein (secured from a condensation product made at 175°) had changed from 178–179° to 247–249° upon standing in a stoppered test-tube. When a large amount of the crystals obtained by the Bischoff and Adkins method was heated in a capillary tube, it was observed that as soon as the temperature reached 175–178° liquefaction began; this was soon followed by solidification; it was necessary to heat the solid to 247–249° before it melted again. The compound now remained liquid or pasty even after cooling. These results indicate that the crystalline substance obtained through the condensation of diphenic anhydride and resorcinol at 135–150° is apparently the same as that which one of us made by the use of a higher temperature, 175°. Also it is obvious that the melting point of resorcinoldiphenein changes when the material is heated or allowed to stand for a long time. This may be due to isomerization, loss of water or other causes. We intend to study this matter further.

Bischoff and Adkins stated that acetylation of their resorcinol-diphenic anhydride condensation product (by heating with acetic anhydride) yielded a substance which was insoluble in alkalies and that the analogous ketone acid derivative was soluble in alkali. Later Adkins and his associates[6] repeated these statements and implied that one of us had overlooked them when criticizing the work. This differentiation procedure might be valid if one were dealing with homogeneous substances, but it is necessary to remember that the material obtained from the diphenic anhydride condensation is a mixture.

We have treated with acetic anhydride the amorphous reaction mass which we obtained by working at 175°, the material secured by the use of Bischoff and Adkins' procedure, and a mixture containing about 70% of crystalline resorcinoldiphenein and 30% of amorphous ketone acid-resorcinol condensation product. In each case 10 cc. of acetic anhydride was used for 1 g. of solid; heating was continued for four hours at 140°; then the mass was cooled, poured on ice and allowed to stand, with occasional stirring, scratching of the walls of the container and additions of cold water, until a pasty solid appeared. The latter was collected, washed with a small amount of sodium carbonate solution and with water; then the solid was pressed on a porous plate. In every case when the material was stirred with *N* sodium hydroxide solution the latter became yellowish-green; some of the solid remained undissolved. Acidification of the filtered liquid gave a considerable amount of precipitate. These experiments show clearly that the material obtained by acetylating Bischoff and Adkins' reaction product is not entirely insoluble in alkali; the results support the criticisms of the work of these investigators.

Summary

When monomethyl diphenate, mono-ethyl diphenate, dimethyl diphenate and diethyl diphenate were heated with acetic anhydride, each ester remained unchanged. Under similar conditions diphenamic acid was dehydrated in two different ways, giving diphenimide and 1-cyanobiphenyl-10-carboxylic acid; the diamide of diphenic acid was transformed into 2,2′-dicyanobiphenyl, through the loss of two molecules of water. *p,p′*-Dibromodiphenic acid formed an anhydride upon treatment with acetic anhydride; the behavior of this acid is different from that of *p,p′*-dinitrodiphenic acid.

Bischoff and Adkins obtained an amorphous substance by condensing diphenic anhydride with resorcinol at 135–150° in the presence of anhydrous zinc chloride and discussed the product as though it were practically homogeneous. This work has been repeated; it was found that the material is apparently identical with that which one of us secured by working at 175°. It contains two substances, resorcinoldiphenein, which can be obtained in crystalline form, and an amorphous condensation product derived from diphenyleneketone-4-carboxylic acid. Incidentally it was learned that the melting point of resorcinoldiphenein apparently changes when the compound is heated or allowed to stand for a long time. Solutions of pure resorcinoldiphenein in aqueous sodium hydroxide do not show marked fluorescence.

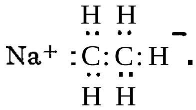
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 8 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND CO.]

THE THERMAL DECOMPOSITION OF SODIUM ETHYL

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

RECEIVED OCTOBER 18, 1928 PUBLISHED FEBRUARY 5, 1929

Application of the octet theory to sodium ethyl leads to the completely polar formula  $\mathrm{Na}^{+}\ :\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\underset{..}{\mathrm{C}}}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\underset{..}{\mathrm{C}}}}}:\mathrm{H}^{-}$. A non-polar or partially polar formula is excluded by the fact that each of these ions has a complete octet. Sharing of electrons between them is therefore impossible.

Sodium alkyls have been prepared in a state of approximate purity by Schlenk and Holtz[1] and their physical properties may be compared with those listed by Lewis[2] as typical of polar substances. They are non-volatile solids which do not melt without decomposition. They are insoluble in petroleum ether and benzene. That they are capable of behaving as true electrolytes has been established by the important work of Hein.[3] Hein showed that solutions of sodium ethyl in zinc ethyl conduct (zinc ethyl is a non-conductor); that the conduction follows Faraday's law; that the ethyl group is actually involved as an anion in the transport of the current; and that it is discharged at the anode with the formation of ethylene and ethane.[4]

The theory and the facts thus agree in all particulars and it seems completely justified to assume that sodium ethyl is composed of sodium ion and ethyl anion. This latter represents one of the possible reactive species of ethyl, and indeed the only one which is capable in a certain sense of being isolated. The spontaneous changes which it undergoes are therefore of considerable theoretical interest. Moreover, these spontaneous changes occur smoothly at temperatures well below 100°, a fact which provides some assurance of the absence of deep-seated secondary reactions.

Wanklyn, who in 1858 prepared $\mathrm{Zn(C_2H_5)_2 \cdot NaC_2H_5}$, the earliest known example of a sodium alkyl, observed that it was decomposed by rather gentle heating with the formation of gases and a residue consisting of a mixture of sodium and zinc. Of this behavior he says,[5] "this reduction of a sodium compound by mere heating is, I think, unique, and is to be regarded as a chemical anomaly."

---

[1] Schlenk and Holtz, *Ber.*, 50, 262 (1927).

[2] Lewis, THIS JOURNAL, 38, 763 (1916).

[3] Hein, Petzschner, Wagler and Segitz, *Z. anorg. allgem. Chem.*, 141, 161 (1924).

[4] When a lead anode was used the product was lead tetra-ethyl.

[5] Wanklyn, Ann., 108, 67 (1858).

The thermal decomposition of sodium ethyl was studied by Schorigin,[6] who observed that the gaseous products consisted exclusively of ethylene and ethane in equivalent amounts. This is, of course, a result which might be expected if the ethyl anion were to lose one electron to the sodium cation with the formation of the ethyl radical. The peculiarity of Schorigin's results which led to a repetition and extension of his experiments was the fact that the first fractions of the gas contained more ethane than ethylene and the last more ethylene than ethane. Such behavior is inconsistent with the assumption that the first products of the reaction are metallic sodium and the ethyl radical.

Schorigin carried out his experiments by mixing mercury ethyl and sodium wire in an atmosphere of nitrogen and immediately heating the mixture until thermal decomposition set in and was complete, the gas being collected over water containing sodium hydroxide and saturated with sodium chloride. The last portion of the hydrocarbon gases was swept into the receiver by a stream of carbon dioxide. In preliminary experiments made by the writers in this way the gas obtained was found to consist chiefly of ethylene. A similar result was obtained when the compound $Zn(C_2H_5)_2 \cdot NaC_2H_5$ was prepared in the pure state and decomposed *in vacuo*, and when sodium ethyl prepared by the method of Schlenk and Holtz was isolated and decomposed *in* vacuo.

All of these methods involved experimental difficulties capable of introducing large errors, and all of the data here presented were obtained by the following procedure.

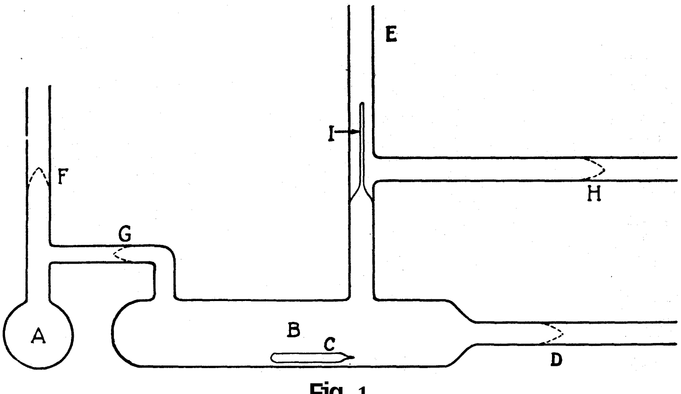


Fig. 1.

Preparation of the Sodium Ethyl.—The tube B containing a known amount of mercury ethyl in the sealed capsule C was sealed at D to a high vacuum line. A large excess of sodium (1–2 g. in all) was placed in the flask A, which was then sealed off at F. The mercury vapor pump was then started and when the pressure had been reduced to less than 0.1 micron, the sodium was distilled into the tube B by heating A with a

---

[6] Schorigin, *Ber.*, 43, 1931 (1910).

free flame, the tube C being cooled by a stream of water falling on B. The sodium condensed as a bright mirror completely covering the walls of B. After the distillation the flask **A** was removed by sealing at G and the tube B was sealed off at D. The tube B was then shaken vigorously to break the capsule C. The thinner portions of the sodium mirror were rapidly blackened by the mercury ethyl: after standing for twelve hours the liquid in the tube had completely disappeared and black granules were present which could readily be broken loose from the surface. After a period of twenty-four to forty-eight hours no trace of mercury ethyl could be found in the tube. These results indicated that mercury ethyl is, under these conditions, quantitatively converted into sodium ethyl.

To obtain the products of the thermal decomposition of the sodium ethyl, the tube B was sealed at E to a Toepler pump and an iron slug was placed in H, which was then sealed. After the system had been completely evacuated, the iron slug was raised by a magnet and allowed to fall on the valve I, thus opening the tube B to the system. The tube B was placed in an oil-bath. The gas was pumped off as it was evolved and collected over mercury.

Analysis of Gases.—The precise analysis of small samples of hydrocarbon gases presents experimental difficulties which have not yet been completely solved. It is thought, however, that none of the analytical results here presented is sufficiently in error to affect any of the conclusions of this study. The apparatus used was that of Bone and Wheeler,[7] which permits the use of 5–20 cc. samples. Hydrogen was determined by direct absorption with Paals' Pd-sol. Ethylene was absorbed by bromine water containing potassium bromide. This reagent slowly attacks ethane also, so that there is some uncertainty in the ethylene : ethane ratios.

Experimental Results

Experiment 7.—Sodium ethyl from 1.312 g. of $Hg(C_2H_5)_2$ and 1.5 g. of sodium was decomposed. Between room temperature and 142°, 213 cc. of gas (S. T. P.) or 94% of the calculated amount was obtained. Of this gas, 6 cc. was present before heating; 7.5 cc. was evolved between 29 and 90° and about 14.5 cc. between 117 and 142°.

Anal. C_2H_4, 84.30; H_2, 0.24; C_2H_6 (by contraction), 14.95; C_2H_6 (by absorption), 14.97; total, 99.51: C/A, 1.248; C_2H_4/C_2H_6, 5.63.

$$C/A = \frac{\text{Contraction in volume due to combustion}}{\text{Contraction in volume due to absorption by KOH}} = \frac{H_2O}{CO_2}$$

Calcd. for ethane, 1.250.

At 142° pumping was continued until no more gas was evolved. The oil-bath was then removed and the tube heated with a free flame. Gas was again copiously evolved. In all 107.5 cc. of gas (S. T. P.) was collected. This gas proved to be nearly pure hydrogen.

Anal. (1) C_2H_4 (by Br absorption) 1.11; H_2 (by Pd absorption) 97.65; C_2H_6 (by difference) 1.24; C_2H_4 (by Br absorption) 1.24. (2) By combustion and absorption, H_2, 97.70; C_2H_6, 1.22.

---

[7] See Grice and Paymen, Fuel *Science* Practice, July, 1924.

Although the C/A ratio indicated the absence of higher hydrocarbons, a special search for butane was made as follows: 150 cc. of the gas of Experiment 7 was placed in communication with an evacuated bulb of 10 cc. capacity which was immersed in a mixture of carbon dioxide snow and acetone. No liquid was observed to condense. The bulb while still in the freezing mixture was sealed off and after warming was opened under mercury so as to transfer the gas directly to the gas analysis apparatus. Some air was admitted during this process. Ethane found by contraction was 11.52 and by absorption 11.80%, the ratio being 1.218. Assuming no experimental error in the analysis, this would indicate the presence of about 0.03% of butane in the original sample.

Experiment 8.—The following experiment is typical of those in which the gas was collected in a series of fractions and each fraction analyzed separately: 0.635 g. of mercury ethyl; 1.0 g. of sodium.

Frac.	Temp. of bath, °C.	Vol. of gas, cc.	C_2H_4	C_2H_6		Total	C/A	$\frac{C_2H_4}{C_2H_6}$
				By contr.	By abs.			
1[a]	20	3	26.87	69.50	67.50	94.37	1.29	0.41
2	90	26.0	74.10	24.98	25.50	49.60	1.225	2.91
3	90	16.2	85.70	13.90	13.71	99.41	1.267	6.25
4	90	18.5	88.20	11.30	11.24	99.64	1.257	7.85
5	91	16.4	89.60	9.78	9.80	99.40	1.247	9.14
6	90	20.0	89.40	10.03	10.05	99.40	1.248	8.90
7	90–150	8.9	86.85	12.17	11.62	99.43	1.312[b]	7.48

Total, 109.0 cc. = 102.6 cc. (S. T. P.) or 94% of calcd. amount.

[a] Large experimental error owing to small volume of gas.

[b] Including 0.96% of H_2.

Discussion of Results

The analytical data indicate the presence of not more than traces of any other substances than ethylene and ethane in the gases evolved below 150°. Repeated qualitative tests for acetylene were negative and the data of Expt. 7 indicate the absence of higher hydrocarbons.

The data of Expt. 7 show that the gas formed between 25 and 142° consists of ethylene and ethane in the ratio 5.6:1 and that after the reaction has completely stopped at 142°, large amounts of hydrogen are evolved on heating to much higher temperatures. The only obvious way of accounting for this is to suppose that the principal reaction is the transformation of sodium ethyl into ethylene and sodium hydride. The sodium hydride then decomposes at higher temperatures with the liberation of hydrogen.

$$NaC_2H_5 \longrightarrow NaH + C_2H_4 \qquad (1)$$
$$2\,NaH \longrightarrow 2\,Na + H_2$$

Using the polar formula given above, this reaction involves simply the elimination of the unshared electron pair of the ethyl anion together with one of the protons-as hydride ion.

In this connection it is interesting to observe that Jolibois[8] found that both $Mg(C_2H_5)_2$ and C_2H_5MgI decompose at 175° with the formation of ethylene, leaving a residue of MgH_2.[9]

To account for the presence of ethane, one may suppose that the following reaction occurs

$$2\ NaC_2H_5 \longrightarrow Na_2C_2H_4 + C_2H_6$$

This reaction involves simply the transfer of a proton from one ethyl anion to another. The first ion thus becomes a doubly charged anion and the second the neutral molecule, ethane. If one regards ethane as a very weak polybasic acid, this reaction finds many analogies. Thus, $NaOHCH_2$-CH_2OH on heating is converted into $NaOCH_2CH_2ONa$ and $HOCH_2$-CH_2OH.

The data of Expt. 8 show that the gas which is slowly formed at ordinary temperature contains more ethane than ethylene,[10] and there appears to be no simple and obvious way to account for this other than by the equation represented above.

Some idea of the fate of the $Na_2C_2H_4$ may be obtained from a study of the data in Expt. 7. These data show

Sodium ethyl used = 0.01015 mole
H_2 found 105 cc. = 0.00469 mole
C_2H_4 found 180 *cc.* = 0.00804 mole
C_2H_6 found *33 cc.* = 0.00147 mole
Deficit = 0.00064 mole

The number of atoms of hydrogen thus considerably exceeds the number of moles of ethylene, and the total ethane and ethylene lacks 6% of accounting for all of the sodium ethyl. These facts may be accounted for by assuming the following changes

$$\begin{array}{ll}
4\ NaC_2H_5 & \longrightarrow 2\ Na_2C_2H_4 + 2\ C_2H_6 \\
2\ Na_2C_2H_4 & \longrightarrow C_2H_6 + Na_2CHCHNa_2 \\
Na_2CHCHNa_2 & \longrightarrow 2\ NaH + NaCCNa \\
\hline
4\ NaC_2H_5 & \longrightarrow 3\ C_2H_6 + H_2 + 2\ Na + NaCCNa
\end{array}$$

In this series of reactions, which resulted in the formation of 0.00147 mole of ethane, there would be formed 0.00049 mole of sodium acetylide while the carbon deficit would require 0.00064 mole. Unfortunately, no test on the residue for sodium acetylide was made. It was, however, observed, after no more gas was produced by strongly heating the residue, that the admission of air to it caused a brilliant flash of fire. Corresponding to the ethane, there would also be formed 0.00049 mole of hydrogen. When this is subtracted from the 0.00469 mole of hydrogen found, one obtains 0.00420 mole, whereas the 0.00804 mole of ethylene found would require, in accordance with Equation 1, 0.00402 mole. The agreement is all that could be expected from data of this type.

---

[8] Jolibois, Compt. rend., 155, **353** (1912).

[9] Jolibois makes no mention of the presence of any ethane in this gas.

[10] This has been repeatedly verified in other experiments not reported here,

The precise verification of these relationships must await more elaborate experiments, which cannot be performed at this time.

The manner in which the ethylene : ethane ratios changed from less than 1 to more than 9 in successive fractions and then fell off again toward the end clearly indicates the presence of a series of successive reactions or of simultaneous reactions with different temperature coefficients.

One simple and quite obvious reaction finds no place in the above scheme

$$NaC_2H_5 \longrightarrow Na^+ + C_2H_5^-$$

In this reaction the ethyl anion loses one of its unshared electrons to the sodium ion and is converted into the ethyl radical which may then undergo disproportionation or polymerization. It seems possible that the ethyl anion may, under certain conditions, behave in this way (cf. the work of Hein referred to above), and, assuming the correctness of Schorigin's results, this reaction might completely describe the thermal decomposition of sodium ethyl. This reaction requires, however, that ethane and ethylene be formed in precisely equivalent amounts. In all experiments made by the writers with sodium ethyl prepared by various methods, the ethane constituted only a relatively small fraction of the gas evolved and the nature of the data indicates that only a small part of it could have been formed by this reaction.

Summary

1. Mercury ethyl reacts completely with an excess of sodium *in vacuo* with the formation of sodium ethyl.

2. The thermal decomposition of sodium ethyl (in the presence of sodium and mercury) begins very slowly at room temperature and is quite rapid at 100°.

3. The gas formed by the thermal decomposition of sodium ethyl at temperatures in the neighborhood of 90–100° consists of ethylene and ethane in the ratio of about 85 to 15. Sodium hydride is found in the residue. The principal reaction is, therefore, $NaC_2H_5 \longrightarrow NaH + C_2H_4$.

4. The gas formed by the spontaneous decomposition of sodium ethyl at ordinary temperature contains more ethane than ethylene. This is supposed to be due to the reaction $2NaC_2H_5 \longrightarrow Na_2C_2H_4 + C_2H_6$. The analytical data furnish some information concerning the fate of the $Na_2C_2H_4$.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PREPARATION OF ZINC ALKYLS AND THEIR USE IN THE SYNTHESIS OF HYDROCARBONS

BY C. R. NOLLER

RECEIVED OCTOBER 23, 1928 PUBLISHED FEBRUARY 5, 1929

In attempting to prepare in considerable quantity the lower hydrocarbons of the type R_4C, several possible methods were investigated. Since the most promising method seemed to be by way of the Grignard reagent, this was tried first, but a number of difficulties were encountered. When a primary alkylmagnesium halide is allowed to react with a tertiary alkyl halide, the reaction is slow and incomplete, the yield is low due to the removal of halogen acid, and higher boiling products are formed from which it is difficult to separate the desired product. Furthermore, if the hydrocarbon has a high vapor pressure, it is difficult to separate it from the ether, which is always present even though a portion is distilled before carrying out the reaction with the alkyl halide. The same difficulties arise if a tertiary alkylmagnesium halide is treated with a compound such as diethyl sulfate, and in addition the yield of Grignard reagent is low (40–45% using the tertiary chlorides, 12–15% using tertiary bromides). Attempts to prepare these hydrocarbons by the Wurtz reaction from a mixture of tertiary and primary halides were entirely unsuccessful. These facts led to an investigation of the method by which these compounds were first prepared, namely, through the use of zinc alkyls. During the course of this work, several improvements in the preparation and manipulation of zinc alkyls have been made.

Preparation of Zinc Alkyls

There are four chief objections to the use of zinc alkyls for synthetic purposes. 1. They are spontaneously inflammable. 2. The preparation of the zinc–copper couple by reduction of a mixture of zinc dust and copper oxide cannot be performed on a large scale. 3. The process is expensive because of the necessity of using alkyl iodides rather than the bromides. 4. With the exception of zinc methyl and zinc ethyl, the yields are low. A fifth consideration that has done much to prevent their use is that for most purposes they can be replaced by the alkylmagnesium halides.

The objection to the use of zinc alkyls on the grounds of spontaneous inflammability was overcome by Blaise,[1] who worked with solutions of alkyl zinc iodides in toluene and in petroleum fractions. Here, however, it was necessary to use ethyl acetate to bring about the reaction, thus introducing a low boiling liquid, which is often objectionable. Furthermore, the exact quantities of alkyl zinc halide could be determined only by anal-

---

[1] Blaise, *Bull. soc. chim.*, [4] **9**, 1 (1911).

ysis. In the present investigation it was found that by dissolving the pure zinc alkyls in an equal weight of a solvent of the desired boiling point, for example, toluene, xylene or tetralin, the solutions could be readily handled in the open air and poured from one flask to another without danger of ignition. Moreover, in using the zinc alkyls, the presence of a solvent invariably gave better yields than when the reactions were carried out in the absence of a solvent.

Various methods of preparing the zinc for the reaction have been used. The best yields of zinc alkyls have been obtained with the zinc–copper couple of Gladstone and Tribe[2] as prepared by Lachman.[3] This method consists of mixing zinc dust with about 10% of its weight of powdered copper oxide and heating in a current of hydrogen to incipient fusion. It is rather difficult to heat to just the right temperature and almost impossible to carry the method out on a large scale. The product must be protected from the air to prevent oxidation. The present work shows, however, that equally good results can be obtained by using fine turnings of an alloy of zinc with from 5 to 8% of copper. This can be readily prepared in the laboratory from zinc and brass turnings in runs of a kilo or more and as much as five kilos made in four hours. Moreover, it will keep indefinitely in a dry, stoppered bottle.

It has been reported in the literature that alkyl bromides do not react to give either zinc alkyls according to the method of Lachman[3a] or alkyl zinc halides, according to the method of Blaise.[1] Job and Reich[4] state that ethyl bromide reacts with the zinc–copper couple in the presence of a catalyst prepared by causing aluminum to react with ethylene bromide. When using this catalyst, however, the reaction requires from six to eight hours for completion. Inasmuch as the reaction of alkyl iodides is very vigorous after it has started and requires continual watching and intermittent cooling, attempts were made to replace a portion of the iodide by the bromide. If an equimolecular mixture of alkyl iodide and bromide is used, the reaction starts easily, proceeds smoothly and if the product is distilled in *vacuo* the yields are equal to those obtained with iodide alone. A smaller proportion of iodide is necessary in preparing the higher zinc alkyls, such as zinc dibutyl, where one may use a mixture of one mole of butyl iodide to three moles of butyl bromide. It is entirely possible, even in the case of zinc ethyl, to start the reaction with the iodide and keep it going by the addition of the bromide, but this requires careful regulation and is not always successful.

The yields of zinc alkyls are greatly increased if the distillation from the crude reaction mixture is carried out under a vacuum. This was early

---

[2] Gladstone and Tribe, *J. Chem. Soc.*, 26, 445, 678, 961 (1873).

[3] (a) Lachman, *Am. Chem. J.*, 19, 410 (1897); (b) 24, 31 (1900).

[4] Job and Reich, *Bull. soc. chim.*, 33, 1424 (1923).

recognized by Gladstone and Tribe,[2] but for some reason, probably because zinc ethyl and zinc methyl are obtained in excellent yields from the iodide by ordinary distillation, they are the only ones who report such a procedure. The advantage of vacuum distillation is markedly brought out when bromides are used. When zinc ethyl is prepared using a mixture of ethyl iodide and ethyl bromide, ordinary distillation gives a yield of 68%, which is increased to 89% on vacuum distillation. It is even more noticeable in the case of the higher zinc alkyls. Thus ordinary distillation using mixed alkyl halides gives only 39% of zinc dipropyl, whereas on vacuum distillation the yield is 86%.

It is interesting to point out a possible course of the reaction using the mixed halides. In one experiment using a mixture of iso-amyl iodide and iso-amyl bromide, the reaction did not go to completion and since the run was of considerable size, the unused alkyl halides were recovered during the distillation. It was expected that since the iodide reacts most readily with the zinc, the unused halide would be the bromide. Actually the recovered halide was practically pure iodide. This might be explained by assuming that the alkyl iodide reacts with the zinc to give zinc alkyl iodide and this in turn reacts with the alkyl bromide to give more of the alkyl iodide.

$$\mathrm{Zn} + \mathrm{RI} \longrightarrow \mathrm{ZnIR}$$
$$\mathrm{ZnIR} + \mathrm{RBr} \longrightarrow \mathrm{RI} + \mathrm{ZnBrR}$$

This suggests that only a small quantity of iodide would be necessary to bring about the reaction. It was found, however, that a considerable concentration of iodide is necessary to keep the reaction going.

The zinc alkyls which were successfully prepared were zinc diethyl, zinc di-n-propyl, zinc di-n-butyl and zinc di-*iso*-amyl. Secondary halides such as iso-propyl and iso-butyl halides gave chiefly gaseous products, presumably the saturated and unsaturated hydrocarbons,[2] and only minute quantities of the zinc alkyl.[5] Cyclohexyl bromide was found to react with the zinc–copper couple at the boiling point of the bromide to give a mixture of cyclohexene and dicyclohexyl. Diethyl sulfate does not react with the couple,

Preparation of Hydrocarbons

Most textbooks of organic chemistry state that hydrocarbons may be prepared by the action of zinc alkyls on alkyl halides and give as a general reaction

$$\mathrm{ZnR_2} + 2\mathrm{R'X} \longrightarrow 2\mathrm{R{-}R'} + \mathrm{ZnX_2}$$

---

[5] Bohm [J. Russ. *Phys.-Chem. Soc.*, 31, 46 (1899); Chem. *Zentr.*, I, 1067 (1899)] claims a yield of 25% of zinc di-isopropyl, while Gladstone and Tribe (ref. *2)* get only gaseous products. Garzarolli-Thurnlackh and Popper [*Ann.*, 223, 168 (1884)] claim a yield of 3541% of zinc di-isobutyl.

The only alkyl halides which we have found to react with the zinc alkyls are the tertiary alkyl halides. Primary and secondary halides and such compounds as diethyl sulfate and allyl bromide could not be made to react under the conditions of the experiment. Moreover, hydrocarbons reported in the literature as prepared by means of zinc alkyls are all prepared from the tertiary halides. Because of their ease of preparation, the chlorides only have been used in the present work.

It has been found that the yields are improved by carrying out the reaction in the presence of an inert solvent of such a boiling point that the product could be separated easily by distillation. Thus the yield of trimethylethylmethane was 18% without using a solvent and 45% using xylene as a solvent. To obtain a product as free from halogen as possible, the solution of alkyl halide is run into a slight excess of the zinc alkyl in the desired solvent.

The temperature used was the lowest that would permit the reaction to run smoothly. It is *absolutely essential* that only a small amount of the halide be added at first and the mixture warmed until the reaction starts. The mixture is then kept at this temperature throughout the reaction. If a considerable amount of the halide is added without the reaction starting, there is danger that the reaction will take place with explosive violence.[6] This would seem to indicate that the reaction is auto-catalytic and it would be interesting to attempt to find catalysts that would allow the reaction to start easily and possibly to proceed at lower temperatures.

In all cases the yields are low (25–51%) but it is believed that this method gives higher yields and purer products with less trouble than any other now available.

Experimental

General Procedure for Preparing Zinc Alkyls.—In a 1-liter round-bottomed flask fitted with a reflux condenser and a heavy stirrer is placed 130 g. (approx. 2 moles) of fine turnings of a zinc–copper alloy containing from 5 to 8% of copper. To this are added 0.5 mole of alkyl iodide and 0.5 mole of alkyl bromide and the mixture is gently refluxed with slow stirring. From twenty to forty minutes after refluxing begins the reaction starts, as is evidenced by the greatly increased rate of refluxing, and the source of heat should be removed. In case the reaction should become too vigorous, the flask is cooled with ice water but only to the point where the reaction is again under control. At the end of half an hour from the time the heat was removed the reaction is usually

---

[6] In one instance the solution of zinc alkyl was cooled in an ice–salt bath and kept at a low temperature whiie the alkyl halide was added. No reaction seemed to take place at first, but shortly and without warning an explosion of such violence took place that it resembled a detonation. An enameled pan containing the ice–salt mixture was crumpled by the force of the explosion. On repeating the experiment on a smaller scale, the same violent reaction took place, though with less destructive force. If, however, the proper precautions are taken to start the reaction, it proceeds smoothly and without any danger whatsoever.

over. The flask is allowed to cool, transferred to a distilling head and' condenser and distilled directly from the reaction flask under a pressure of less than **30** mm. of mercury. The apparatus need not be swept out with an inert gas before starting the distillation but at the end, when the vacuum is released, dry carbon dioxide is admitted to the apparatus instead of air. On redistillation in *vacuo* through a column, practically the entire product boils over a range of **3** to 5°. After weighing the product, an equal weight of the desired dry solvent is added and the solution is ready for use in subsequent reactions.

TABLE I

DATA ON ZINC DIALKYLS

Zinc alkyl	B. p.. °C.	Yield, %
Zinc diethyl[a]	112–117 (atm.)	87–89
Zinc di-n-propyl[b]	3940 (9 mm.)	85–86
Zinc di-*n*-butyl[c]	81–82 (9 mm.)	78–79
Zinc di-iso-amyl[a]	100–103 (12 mm.)	50–55

[a] Frankland, Ann., **85, 360 (1853).** [b] Ref. **2.** [c] *Anal.* Subs., **2.4121: 26.64** cc. of N HCl. Calcd. for $Zn(C_4H_9)_2$: Zn, **36.45.** Found: **36.11.**

General Procedure for Preparing Hydrocarbons.—To a 500-cc. three-necked flask fitted with a reflux condenser, thermometer, dropping funnel and stirrer is added **0.28** mole of zinc **alkyl** dissolved in an equal weight of inert solvent. In the dropping funnel is placed **0.5** mole of tertiary alkyl chloride, also dissolved in an equal weight of

TABLE II

REACTING SUBSTANCES AND PRODUCTS

No.	Reactants			Hydrocarbon produced	Yield, %
	Zinc	Chloride	Solvent		
1	Diethyl	*Tert.*-butyl	Xylene	Trimethylethylmethane[a]	45
2	Di-*n*-propyl	*Tert.*-butyl	Xylene	Trimethylpropylmethane[b]	40
3	Di-n-butyl	*Tert.*-butyl	Tetralin	Trimethylbutylmethane	36
4	Di-iso-amyl	*Tert.*-butyl	Tetralin	Trimethyl-iso-amylmethane[c]	25[d]
5	Diethyl	*Tert.*-amyl	Xylene	Dimethyldiethylmethane[e]	51
6	Di-n-propyl	*Tert.*-amyl	Tetralin	Dimethylethylpropylmethane[f]	24
7	Di-n-butyl	*Tert.*-amyl	Tetralin	Dimethylethylbutylmethane	29

[a] Gorianow, Ann., **165, 107 (1873).**

[b] Markownikow, Ber., **33, 1905 (1900).**

[c] Kishner, J. Russ. *Phys.-Chem. Soc.*, **45,957 (1913);** *Chem. Zentr.*, **II, 2131 (1913).**

[d] In this case the yield is based on a fraction boiling at 115–125°. Other isomers were undoubtedly present in the iso-amyl iodide and bromide used and the fraction boiling at 121–123° was obtained only after several distillations.

[e] Friedel and Ladenburg, Ann., 142, **310 (1867).**

[f] Späth, Monatsh., **34, 1965 (1913).**

PHYSICAL CONSTANTS OF PRODUCTS

No.	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refr.	
				Obs.	Calcd.
1	49.5–50.5	0.6512	1.3675	29.6	28.5
2	80–81	.6778	1.3828	34.4	32.9
3	106–107	.6967	1.3931	39.0	37.4
4	121–123	.7091	1.3997	43.7	41.8
5	86–86.5	.6952	1.3908	34.2	32.9
6	111–112	.7116	1.3998	38.8	37.4
7	137–138	.7304	1.4095	43.3	41.8

solvent. A small amount of the chloride is run into the flask and the mixture is gradually heated until a sharp rise in temperature takes place, indicating that the reaction has started. (Caution: The reaction must get started before a large amount of the chloride has been added or an explosion may result.) More halide is then slowly added, keeping the mixture at the temperature at which the reaction started. At the end of the addition the mixture is decomposed with dilute hydrochloric acid, washed, dried and the hydrocarbon distilled from the solvent through a column. A second distillation gives a product boiling over a range of 1 to 2°. A considerable amount of gas or a low-boiling fraction is always obtained, either during the reaction or the distillation. This was not investigated but is probably a mixture of saturated and unsaturated hydrocarbons.

Summary

1. Improvements in the preparation and manipulation of zinc alkyls are given.
2. The zinc alkyls have been used to prepare a number of hydrocarbons of the type R_4C.

EVANSTON, ILLINOIS

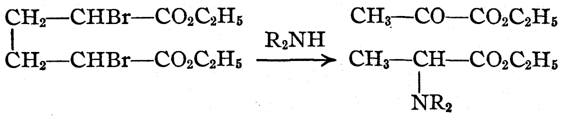
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE CLEAVAGE OF DIETHYL ALPHA,ALPHA'-DIBROMO-ADIPATE BY SECONDARY AMINES[1]

BY REYNOLD C. FUSON AND RAYMOND L. BRADLEY

RECEIVED OCTOBER 31, 1928 PUBLISHED FEBRUARY 5, 1929

It has been shown by von Braun, Leistner and Miinch[2] that diethyl α,α'-dibromo-adipate when treated with certain secondary amines is cleaved in such a way as to give ethyl pyruvate and an amino ester reported by them to be ethyl a-dialkylaminopropionate.



$$\begin{array}{l} CH_2—CHBr—CO_2C_2H_5 \\ | \\ CH_2—CHBr—CO_2C_2H_5 \end{array} \xrightarrow{R_2NH} \begin{array}{l} CH_3—CO—CO_2C_2H_5 \\ \\ CH_3—\underset{\underset{NR_2}{|}}{CH}—CO_2C_2H_5 \end{array}$$

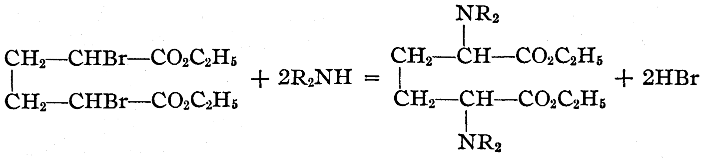
They reported that diethylamine, di-n-propylamine, copellidine and di-iso-amylamine produce the same type of cleavage, yielding in each case ethyl pyruvate and an a-dialkylaminopropionic ester. This list has subsequently been extended by von Braun, Jostes and Wagner[3] to include a number of similar amines of this class. Dimethylamine and piperidine, however, gave no cleavage but were found to react normally to give the corresponding tetra-alkyldiarnino-adipicesters.

---

[1] This work was presented before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 9, 1928.

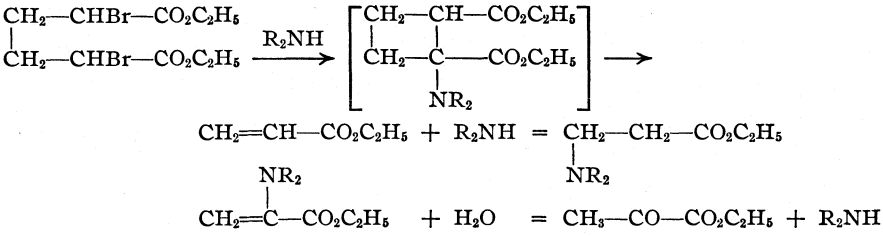
[2] Von Braun, Leistner and Munch, **Ber., 59B, 1950 (1926).**

[3] Von Braun, Jostes and Wagner, *ibid.,* **61B, 1423 (1928).**



$$\begin{array}{l} CH_2-CHBr-CO_2C_2H_5 \\ | \\ CH_2-CHBr-CO_2C_2H_5 \end{array} + 2R_2NH = \begin{array}{l} CH_2-\overset{NR_2}{\overset{|}{C}}H-CO_2C_2H_5 \\ | \\ CH_2-\underset{NR_2}{\underset{|}{C}}H-CO_2C_2H_5 \end{array} + 2HBr$$

In a recent paper Fuson[4] presented a mechanism to explain the apparently novel type of chain rupture, assuming the formation of a cyclobutane derivative as an intermediate compound.



$$\begin{array}{l} CH_2-CHBr-CO_2C_2H_5 \\ | \\ CH_2-CHBr-CO_2C_2H_5 \end{array} \xrightarrow{R_2NH} \left[\begin{array}{l} CH_2-CH-CO_2C_2H_5 \\ |\qquad\quad | \\ CH_2-\underset{NR_2}{\underset{|}{C}}-CO_2C_2H_5 \end{array}\right] \longrightarrow$$

$$CH_2{=}CH-CO_2C_2H_5 + R_2NH = \underset{NR_2}{\underset{|}{C}}H_2-CH_2-CO_2C_2H_5$$

$$CH_2{=}\overset{NR_2}{\overset{|}{C}}-CO_2C_2H_5 + H_2O = CH_3-CO-CO_2C_2H_5 + R_2NH$$

It was pointed out that a dissociation of this hypothetical intermediate into two molecules of ethylenic character, a type of reaction characteristic of cyclobutane derivatives, would yield, respectively, ethyl acrylate and ethyl a-dialkylamino acrylate. The former would be expected to combine with a molecule of the dialkylamine to give ethyl β-dialkylaminopropionate; the acrylic ester would be hydrolyzed to ethyl pyruvate.

The proposed mechanism agreed with the findings of von Braun, Leistner and Münch except in that it postulated the formation of β-dialkylpropionic esters instead of the a-esters reported. This difficulty was cleared away when it was shown that in the reaction between diethyl-α,α-dibromoadipate and diethylamine the amino ester obtained is actually ethyl β-diethylaminopropionate and not the a as reported by von Braun and his co-workers.[3]

The importance of this point in relation to the theory is such that it has been checked also in the case of di-n-propylamine. As was to be expected, ethyl β-di-*n*-propylaminopropionate was obtained and not the corresponding a-ester. The position of the amino group was established as in the previous case by a mixed melting-point determination of the methiodide of the amino ester with that of the authentic specimen. The amount of cleavage in the case of di-n-propylamine was 85%.

Von Braun and his co-workers believe that the tendency of a given amine to produce the cleavage is dependent on the form of the amine. Thus they point out that while piperidine does not produce cleavage the pipecolines and copellidine do so. This, they say, is because piperidine is dish-shaped and may be inserted into the adipic ester molecule without

---

[4] Fuson, THIS JOURNAL, 50, 1444 (1928).

disrupting it. Amines which cause cleavage do so, it is asserted, because of their more three-dimensional form.

On the basis of the proposed cyclobutane mechanism for the cleavage, it is difficult to understand why the slight difference between piperidine and the pipecolines should have such a profound effect on the tendency to cause cleavage. The action of piperidine has, therefore, been re-examined.

It has been shown that, contrary to the findings of von Braun and his students, cleavage takes place, giving in addition to the diethyl α,α'-dipiperidino-adipate reported by them the cleavage products ethyl pyruvate and ethyl-β-piperidinopropionate. The former, owing presumably to the fact that it is readily hydrolyzed by water, was obtained in a relatively small amount. The yield of ethyl-β-piperidinopropionate, however, was 75% of the theoretical. It was proved to be the β- and not the α-amino ester by comparing its methiodide with an authentic specimen.

Experimental

***Meso*-diethyl-α,α'-dibromo-adipate and Di-*n*-propylamine.**—The method of von Braun, Leistner and Munch[2] was used. A mixture of 36 g. (0.1 mole) of *meso*-diethyl-α,α'-dibromo-adipate and 60.6 g. (0.6 mole) of di-n-propylamine was heated gently until reaction had begun. The reaction was allowed to proceed under its own heat until it had moderated somewhat. The mixture was then heated for five hours on the steam-bath, cooled and shaken with ether and excess dilute hydrochloric acid. The ether layer was removed, dried over sodium sulfate and distilled. Only a small amount of ethyl pyruvate was obtained.

The aqueous layer was made alkaline with sodium hydroxide and extracted thoroughly with ether. The ether extract was dried over sodium sulfate and distilled. The ethyl-β-di-*n*-propylaminopropionate distilled at 112–114° (20 mm.). (This base was prepared by von Braun, Leistner and Munch, who identified it as ethyl-α-di-*n*-propylaminopropionate. They reported a boiling point of 102–104° (12 mm.) for the base and a melting point of 76° for its methiodide.) The yield was 15 g. or 85% of the theoretical. The identity of the ethyl-β-di-*n*-propylaminopropionate obtained was confirmed by means of a mixed melting-point determination. When its methiodide was mixed with that of an authentic specimen of the base (preparation described below) there was no depression of the melting point.

Ethyl-β-di-*n*-propylaminopropionate.—Ten g. of di-n-propylamine dissolved in dry benzene was treated with 3 g. of ethyl-β-chloropropionate. The mixture was heated on the steam-bath for an hour, cooled and washed with water to remove the di-n-propylamine hydrochloride. The benzene solution was dried and distilled. The ethyl-β-di-*n*-propylaminopropionate boiled at 112–114° (20 mm.). Its methiodide melted at 76°.

***Meso*-diethyl-α,α'-dibromo-adipate** and Piperidine.—The method of von Braun and Münch[5] was used but inasmuch as the results were considerably different, the exact procedure is indicated. Thirty g. of *meso*-diethyl-α,α'-dibromo-adipate was heated under reflux for one and one-half hours with 50 g. of piperidine. The reaction was very vigorous and the flask had to be cooled somewhat at the beginning. The reaction products were isolated in the manner indicated above in the experiment with di-n-propylamine. Only a small amount of ethyl pyruvate was isolated. It was identified

---

[5] Ref. 2, p. 1947.

by means of a mixed melting-point determination with its phenylhydrazone (m. p. 118°) and that of an authentic specimen of ethyl pyruvate.

Of the basic product twelve g. distilled at 114–116° (22 mm.) and was shown (see below) to be ethyl-β-piperidinopropionate; yield, 75% of the theoretical; d_{20}, 0.927.

Anal. Calcd. for $C_{10}H_{19}O_2N$: C, 64.85; H, 10.35. Found: C, 64.6; H, 10.0.

The methiodide melted at 100–102°. A mixed melting-point determination with the methiodide prepared from a known sample of the piperidino ester, whose preparation is described below, served to identify the compound.

The residue from the distillation proved to be diethyl-α,α'-dipiperidino-adipate. Four g. of this compound was isolated After four recrystallizations from ether and one from petroleum ether the compound melted sharply at 94° (von Braun and Münch give 99° as the melting point).

Anal. Calcd. for $C_{20}H_{36}O_4N_2$: C, 65.2; H, 9.8. Found: C, 65.3; H, 9.8.

Ethyl-β-piperidinopropionate.—Seventeen g. of piperidine dissolved in 50 g. of dry benzene was refluxed with 6 g. of ethyl-β-chloropropionate. The product distilled at 113–116° (22 mm.). The methiodide melted at 100–102°.

Summary

Meso-diethyl-α,α'-dibromo-adipate is cleaved by piperidine to give a 75% yield of ethyl-β-piperidinopropionate.

Di-n-propylamine gives ethyl-P-di-n-propylaminopropionate in a yield of 85%.

The identity of ethyl-β-piperidinopropionate and of ethyl-β-di-*n*-propylaminopropionate has been established by mixed melting-point determinations of the methiodides with authentic specimens.

URBANA, ILLINOIS

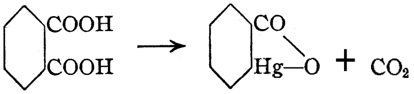
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE REPLACEMENT OF CARBOXYL BY MERCURY IN CERTAIN 3-SUBSTITUTED PHTHALIC ACIDS. PRELIMINARY PAPER

BY FRANK C. WHITMORE AND PAUL J. CULHANE

RECEIVED NOVEMBER 2, 1928 PUBLISHED FEBRUARY 5, 1929

It has long been known that the treatment of phthalic acid with mercuric acetate gives an o-mercurated benzoic acid.[1] The present study was undertaken to determine the mechanism of the mercuration and to find the effect of substituents on the reaction.

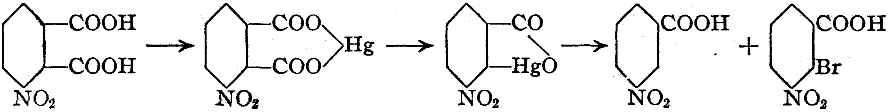


The first step in the reaction is the formation of an insoluble mercuric salt, as is the case in the mercuration of benzoic acid. The mercuric phthalate may then lose carbon dioxide with the replacement of the carboxyl by mercury. Another alternative is that the mercuric salt under

---

[1] Pesci, *Atti accad. Lincei,* [5] *10,* 1, 362 (1901).

the influence of heat may mercurate the benzene ring ortho to one of the carboxyls as happens in the mercuration of benzoic acid. The product would be a 3-mercurated phthalic acid which, on losing carbon dioxide, would give the observed product, o-mercurated benzoic acid. Working with phthalic acid it is impossible to distinguish between these mechanisms. Consequently, 3-substituted phthalic acids were studied. The mercuration of 3-nitrophthalic acid gave a nearly quantitative yield of a mercury compound which reacted with hydrochloric acid to give *m*-nitrobenzoic acid and with bromine to give 2-bromo-3-nitrobenzoic acid. This proves the reaction to be actually a replacement of carboxyl by mercury. In this case the replacement was limited to the 2-carboxyl. If mercuration had preceded the loss of carbon dioxide, the products would have been either m-nitrobenzoic acid and 2-bromo-5-nitrobenzoic acid or *o*-nitrobenzoic acid and 2-nitro-5-bromobenzoic acid. The actual course of the reactions was as follows.



Similar results were obtained with 3-bromophthalic acid and 3-chlorophthalic acid. In each case mercury compounds were obtained which gave 3-halogen benzoic acids on treatment with hydrochloric acid. 3-Iodophthalic acid reacted with mercuric acetate to give mercuric iodide and a complex organic mercury compound from which no substituted benzoic acid was obtained.

Experimental Part

Reaction of Sodium 3-Nitrophthalate with Mercuric Acetate.—A warm filtered solution of 211 g. of 3-nitrophthalic acid in 800 cc. of water and 80 g. of sodium hydroxide was mixed in a 3-liter long-necked flask with a hot solution of 350 g. of mercuric acetate in 700 cc. of water and 50 cc. of glacial acetic acid. The flask was provided with a reflux condenser and placed in an oil-bath which was gradually heated to 170°. Evolution of carbon dioxide commenced when this temperature was reached. After heating for seventy hours at 170°, no more carbon dioxide was evolved and a small test sample of the mixture was completely soluble in sodium hydroxide solution. The solid product was washed with water and with alcohol and dried to constant weight at 110°; yield of anhydro-2-hydroxymercuri-3-nitrobenzoic acid, 330 g. or 90%.

Anal. Subs., 0.1987, 0.2010: Hg, 0.1071, 0.1118. Calcd. for $C_7H_3O_4NHg$: Hg, 54.9. Found: 53.9, 55.6.

The analysis was made by the gold crucible method.[2] As is often the case with nitro compounds considerable difficulty was experienced because of the somewhat explosive decomposition of the mercury compounds.

Action of the Mercury Compound with Hydrochloric Acid.—A suspension of 36.6 g. of the mercury compound from 3-nitrophthalic acid, 100 cc. of concd. hydrochloric

---

[2] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, 1921, p. 365.

acid and 50 cc. of water was heated under reflux for twenty minutes. Complete solution resulted. The crystals obtained by cooling the mixture were crystallized three times from hot water; m. p. 141–143'. Addition of a known sample of m-nitrobenzoic acid did not lower the melting point.

Action of **Fuming** Nitric Acid.—Anhydro-2-hydroxymercuri-3-nitrobenzoic acid dissolved completely in a large excess of hot fuming nitric acid. The mercury was not removed from organic combination even after refluxing for five hours. Dilution of the mixture precipitated unchanged material. The filtrate gave no test for inorganic mercury either with sodium hydroxide or hydrogen sulfide.

Action of Halogens on Anhydro-2-hydroxymercuri-3-nitrobenzoic Acid.—A solution of bromine in carbon tetrachloride was without action on the anhydro compound. On being stirred with an aqueous solution of potassium bromide and bromine, reaction took place, as evidenced by the disappearance of color. Since the reaction was slow, the following procedure was adopted. The anhydro compound (3.7 g.) was heated under reflux with 10 cc. of 2 molar potassium perbromide solution. This represented a 100% excess of bromine. The powdered mercury compound went into solution within two minutes. On cooling, bromine separated from the mixture although before adding to the mercury compound all the bromine had been in solution. The bromine was removed by extraction with chloroform. The aqueous solution was diluted to about 100 cc. and acidified with 5 cc. of concd. hydrochloric acid. The resultant crystalline precipitate was filtered and dried. It contained no mercury and melted at 186–188'. A mixed melting-point determination with 2-bromo-3-nitrobenzoic acid obtained by A. F. Holleman[3] by the nitration of o-bromobenzoic acid showed the identity of these materials.

By a similar process 2-iodo-3-nitrobenzoic acid, melting at 204–205.5°, was obtained.

Treatment with chlorine gave 2-chloro-3-nitrobenzoic acid melting at 180–182". Holleman gives the melting point as 185°.[4]

Mercuration of 3-Bromophthalic Acid.—A solution of 10 g. of 3-bromophthalic acid (m. p. 186.5–189") in 100 cc. of water containing 4 g. of anhydrous sodium carbonate was mixed with a solution of 13 g. of mercuric acetate in 100 cc. of water and 5 cc. of glacial acetic acid The resulting precipitate was filtered, washed and dried. The precipitated mercuric salt was suspended in 200 cc. of water and heated under a reflux condenser for fifty-three hours. At that point the mixture was completely soluble in sodium hydroxide. The entire mixture was made alkaline with sodium hydroxide, filtered from a slight residue and acidified with acetic acid. The precipitate formed was always obtained in a gelatinous form which seemed impossible to purify. Boiling this material with concd. hydrochloric acid gave m-bromobenzoic acid melting at 150–154°. Addition of known m-bromobenzoic acid did not lower the melting point.

Mercuration of 3-Chlorophthalic Acid.—3-Chlorophthalic acid (m. p. 185–187°) was mercurated in a similar way. Treatment of the mercury compound with hydrochloric acid gave m-chlorobenzoic acid melting at 150.5–154°. Addition of known m-chlorobenzoic acid failed to lower the melting point.

Summary

1. 3-Nitro-, 3-bromo- and 3-chlorophthalic acids react with mercuric acetate on long refluxing to form carbon dioxide and products containing mercury in place of the 2-carboxyl.

---

[3] Holleman and de Bruyn, *Rec. trav. chim.*, 20,211 (1901).

[4] **Ref.** 3, p. 209.

2. The mercury compound from 3-nitrophthalic acid is obtained in good yield and reacts with bromine and with iodine to give good yields of the otherwise difficultly obtainable 2-bromo-3-nitrobenzoic acid and 2-iodo-3-nitrobenzoic acid.

3. Anhydro-2-hydroxymercuri-3-nitrobenzoic acid can be refluxed with fuming nitric acid without breaking the C-Hg linkage. On the other hand a short heating with concd. hydrochloric acid removes the mercury completely from the organic molecule.

4. The results obtained with the 3-substituted phthalic acids show that the mercuration reaction consists in the replacement of the 2-carboxyl by mercury.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE PLAUT LABORATORY OF LEHN AND FINK, INC.]

THE PREPARATION OF CERTAIN CHLORO AND BROMO DERIVATIVES OF 2,4-DIHYDROXYDIPHENYLMETHANE AND -ETHANE AND THEIR GERMICIDAL ACTION[1]

BY EMIL KLARMANN AND JOHN VON WOWERN

RECEIVED NOVEMBER 6, 1928 PUBLISHED FEBRUARY 5, 1929

Introduction

The introduction of aryl groups into the nucleus of resorcinol leads to compounds showing a very pronounced germicidal action.[2] It has been shown that of the three aryl groups, *viz.*, benzyl, phenylethyl and phenylpropyl, the introduction of the second produces the most active aryl derivative of resorcinol, the phenol coefficient of which was reported as being 41, against B. *typhosus*.[3]

It is well known that halogen substitution of phenol and its alkyl derivatives leads to compounds, the germicidal potency of which is very considerably greater than that of the unsubstituted compounds. While the germicidal action increases with the number of halogen atoms introduced (one molecule of pentabromophenol has the same effect upon B. *diphtheriae* as *500* molecules of phenol), the toxicity first drops but later rises again. Thus monohalogen phenol is less toxic than phenol, while the general toxicity of trihalogen phenol approximately equals that of phenol itself; tetra- and pentahalogen phenol derivatives are more toxic than phenol.[4]

[1] Presented in part before the Division of Biological Chemistry at the meeting of the American Chemical Society in Swampscott, Massachusetts, September, 1928.

[2] E. Klarmann, THIS JOURNAL, 48,791 (1926).

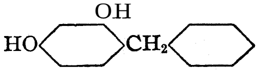
[3] E. Klarmann, *ibid.*, 48,2358 (1926).

[4] *R.* Koch, Mitt. *Kais. Gesundheitsamt, 1,* 234 (1881); H. Bechhold and P. Ehrlich, *Z. physiol. Chem., 47,* 173 (1906); K. Laubenheimer, "Phenol und seine Derivate als Desinfektionsmittel." Berlin-Wien. 1909.

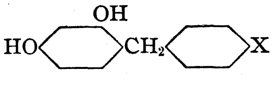
In continuing our work on the relationship between the germicidal action and chemical constitution we have taken another factor into consideration, *k.* ,inactivation of the disinfectant in the presence of organic matter (particularly of protein character), which may be regarded as eminently important from both a practical and theoretical viewpoint. It is well known that many chemicals which are strong germicides in the absence of organic matter may be greatly or even totally inactivated in its presence. Bechhold and Ehrlich found that the very pronounced germicidal efficacy of polyhalogen substituted phenols and phenol derivatives is greatly reduced in the presence of serum; such reduction need not necessarily be accompanied by a precipitation of the protein. On the other hand, there is evidence that the inactivation by organic matter of unsubstituted phenol or cresol takes place to a much less degree.

Discussion

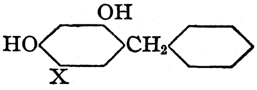
We were interested in determining the influence of monohalogen substitution upon the germicidal action of certain aryl derivatives of resorcinol. Considering the structural formula, e. g., of 2,4-dihydroxydiphenylmethane



the halogen may be introduced either into the benzene nucleus which bears the hydroxyl groups or into the unsubstituted one. In this paper we have considered halogen substitution in the positions 4' and 5, respectively; thus the compounds studied belong to the two types



or



wherein X stands for either Cl or Br. The difference in germicidal action resulting from such substitution is indicated in Table I. The figures under I are phenol coefficients determined according to a modified Rideal-Walker procedure using B. typhosus, under II the same in the presence of standard organic matter, under III phenol coefficients against Staphylococcus pyogenes aureus, under IV the same as under III in the presence of organic matter.

TABLE I

DIFFERENCES IN GERMICIDAL ACTION

	I	II	III	IV
2,4-Dihydroxydiphenylmethane	18.3	14.5	11.3	7.3
5-Chloro-2,4-dihydroxydiphenylmethane	48.2	36.0	36.7	19.6
4'-Chloro-2,4-dihydroxydiphenylmethane	63.1	27.1	40.1	16.7
5-Bromo-2,4-dihydroxydiphenylmethane	37.3	15.7	44.6	18.3
4'-Bromo-2,4-dihydroxydiphenylmethane	54.8	18.9	51.4	13.6

It appears that the presence of halogen very considerably enhances the germicidal effect; the introduction of the halogen into the nucleus which bears the hydroxyl group leads to derivatives with a lower germicidal potency than substitution in p'-position. There is no very distinct difference between B. *typhosus* and Staph. *pyog. aureus;* this fact tends to indicate that the substances dealt with may probably be regarded as general disinfectants rather than specifics.

Organic matter causes a very considerable reduction of germicidal action of the halogen substituted derivatives (in all cases but two, more than 50%); in contrast to this the inactivation of the unsubstituted 2,4-dihydroxydiphenylmethane is much less pronounced.[5]

We attempted to extend our investigation to the corresponding halogen derivatives of 2,4-dihydroxydiphenylethane. The germicidal action of this compound is indicated in Table II.

TABLE II

GERMICIDAL ACTION OF 2,4-DIHYDROXYDIPHENYLETHANE

	I	II	III	IV
2,4-Dihydroxydiphenylethane	40.8	16	22.1	8.5

The figures under I, II, III and IV correspond with those under the respective headings in Table I. It appears that the presence of organic matter impairs the germicidal action of the 2,4-dihydroxydiphenylethane

---

[5] While this work was in progress a paper was published by Bettylee Hampil, *J. Infectious Diseases,* ***43,*** *25* (1928), according to which the disinfectant action of the higher alkylresorcinols is also very considerably impaired by organic matter, *e. g.,* about 70% in the case of hexylresorcinol and more than 80% in that of heptylresorcinol at 37°. Great differences were also found depending upon the kind of peptone used in compounding the "organic matter." The present bacteriological concept of "organic matter" is rather vague from a chemical viewpoint. Both constituents of the so-called "organic matter," required by certain bacteriological methods for standardization of disinfectants, *viz.,* gelatin and peptone, represent products of partial hydrolysis of protein and probably consist of a mixture of amino acids, polypeptides and amino acid anhydrides which will differ qualitatively and quantitatively depending upon the initial material and the method and duration of the protein hydrolysis.

We assume that the impairment of disinfectant action of phenols, polyphenols and their derivatives is due to the fixation of their hydroxyl group or groups by means of secondary valencies by a reactive group in protein (NH_2, possibly COOH, OH, NH, SH). The stability of this, what may be termed additive (molecular) compound under the conditions of the bacteriological experiment, is regarded as one factor which influences the extent to which the impairment of the disinfectant action takes place. It is obvious that this idea of the impairment of disinfecting action by reactive groups in proteins may be used in a hypothetical explanation of the disinfecting action proper, since it is possible that the reactive groups in "organic matter" which hinder the disinfecting action may resemble those which attach the disinfecting chemical to the microorganism; this is probably the first step in disinfection.

We expect to continue our investigations with the view of contributing experimental evidence in support of this theory.

to a much greater extent than that of the corresponding methane derivative. We also succeeded in obtaining the 5-chloro and bromo derivatives of 2,4-dihydroxydiphenylethane but experienced great difficulties in their bacteriological investigation because of the insolubility of these compounds.

The synthesis of the 4'-halogen substituted derivatives of 2,4-dihydroxydiphenylmethane was carried out according to a method applied by one of us for the preparation of 2,4-dihydroxydiphenylmethane proper, *viz.*, condensation of *p*-chloro- or p-bromobenzonitrile with resorcinol in the presence of dry hydrogen chloride, according to Hoesch,[6] transformation of the 4′-halogen-2,4-dihydroxybenzophenone-imide hydrochloride into the 4′-halogen-2,4-dihydroxybenzophenone and reduction of the latter with amalgamated zinc and hydrochloric acid to the 4′-halogen-2,4-dihydroxydiphenylmethane. Direct condensation of the halogen benzyl chloride with resorcinol in nitrobenzene solution in the presence of anhydrous aluminum chloride may also be used for the synthesis of these compounds.

The 5-halogen derivatives of 2,4-dihydroxydiphenylmethane and -ethane were obtained by direct action of sulfuryl chloride or of bromine upon the respective compounds.

Experimental Part

A. Chemical

Preparation of 4′-Chloro-2,4-Dihydroxydiphenylmethane, $C_6H_3(OH)_2CH_2C_6H_4Cl$.—This compound was prepared according to the following two methods.

Method I.—Seventy g. of resorcinol, which was previously dried at 100° for a period of twelve hours, and 50 g. of anhydrous aluminum chloride were dissolved in 300 g. of freshly distilled, dry nitrobenzene. The solution was placed in a flask fitted with a dropping funnel and connected with an air condenser and a calcium chloride tube. A solution of 50 g. of *p*-chlorobenzyl chloride in 100 g. of dry nitrobenzene was added drop by drop under continuous stirring. After addition of the total quantity, the flask was heated on the water-bath and kept at a temperature of 70" for four hours. The resulting dark liquid was poured upon chopped ice and allowed to stand; the watery portion was drawn off and the oil washed with dilute hydrochloric acid and then with water. After addition of an equal volume of ether, the liquid was shaken repeatedly with a 10% solution of sodium hydroxide. The alkaline extract was shaken with ether repeatedly in order to remove the adhering nitrobenzene completely. Then hydrochloric acid was added and the whole boiled for half an hour. The precipitated dark oil was washed with water and distilled in a vacuum at 5 mm. The main part distilled at 200–225° as a heavy oil; by dissolving this in a large quantity of boiling water and cooling, the 4′-chloro-2,4-dihydroxydiphenylmethane crystallized in white needles; yield, 55%. After drying in a micro vacuum desiccator, the melting point is 80.4" (uncorr.). The halogen determination was carried out according to Pregl's micro modification of Carius' method.

Anal. Subs., 4.166 mg.: AgCl, 2.550 mg. Calcd. for $C_{13}H_{11}O_2Cl$: Cl, 15.11. Found: Cl, 15.14.

Method 11.—Sixty g. of dry resorcinol and 50 g. of *p*-chlorobenzonitrile, previously

---

[6] R. Hoesch, *Ber.*, 48, 1122 (1915).

dried in a vacuum desiccator over phosphorus pentoxide, were dissolved in 200 cc. of dry ether and 10 g. of zinc chloride, previously fused and powdered, was added. A current of hydrogen chloride, dried by means of sulfuric acid, was passed through the mixture for a period of about five hours. A heavy oil formed. The vessel was allowed to stand in an ice box for twenty-four hours; then cold hydrochloric acid (15%) was added, whereby the oily keto imide hydrochloride was transformed into a crystalline mass. The crystals were filtered off and washed repeatedly with cold ether in order to remove the unchanged nitrile; yield, 72%.

The 4'-chloro-2,4-dihydroxybenzophenone-imide hydrochloride thus obtained was boiled with approximately 1 liter of water for half an hour, whereby the imide hydrochloride was transformed into the ketone. The latter was recrystallized from water; yield, 65% of the imide hydrochloride. The 4'-chloro-2,4-dihydroxybenzophenone forms pinkish needles which after drying in a micro vacuum desiccator melt at 155° (uncorr.). A solution in dilute alcohol gives a purple coloration with ferric chloride.

This keto compound was reduced by boiling with 150 g. of amalgamated zinc and hydrochloric acid (10%) until a sample of the oil when dissolved in alcohol and diluted with water gave no distinct coloration with ferric chloride. The mixture was shaken with ether, the ether solution washed with dilute hydrochloric acid (2%) and finally with water. The ethereal layer was drawn off, dried with sodium sulfate, the solvent evaporated and the residue distilled in a vacuum at 5 mm. Further purification was carried out as described under Method I; yield, 70% of the keto compound; total yield, 33%.

Preparation of **4'-Bromo-2,4-dihydroxydiphenylmethane, $C_6H_3(OH)_2CH_2C_6H_4Br$.**—This compound was prepared according to the procedure given under Method II. The 4'-bromo-2,4-dihydroxybenzophenone melts at 169° (uncorr.); yield, 89% of the corresponding imide hydrochloride. The 4'-bromo-2,4-dihydroxydiphenylmethane melts at 96° (uncorr.); yield, about 70% of the keto compound; total yield, 45%.

Anal. Subs., 4.227 mg.: AgBr, 2.855 mg. Calcd. for $C_{13}H_{11}O_2Br$: Br, 28.67. Pound: Br, 28.74.

Preparation of **5-Chloro-2,4-dihydroxydiphenylmethane, $C_6H_2(OH)_2ClCH_2C_6H_5$.**—One part of 2,4-dihydroxydiphenylmethane was dissolved in 10 parts of dry ether. The theoretical quantity of sulfuryl chloride was added drop by drop under continuous stirring and cooling. The ether solution was washed with water repeatedly, dried over sodium sulfate, decolorized with Darco and the solvent evaporated. The residue was recrystallized from carbon tetrachloride. The compound crystallizes in white needles which after drying melt at 122° (uncorr.); yield, 51%.

Anal. Subs., 5.785 mg.: AgCl, 3.583 mg. Calcd. for $C_{13}H_{11}O_2Cl$: Cl, 15.11. Found Cl, 15.32.

Preparation of **5-Chloro-2,4-dihydroxydiphenylethane, $C_6H_2(OH)_2ClCH_2CH_2C_6H_5$.**—This compound was prepared by chlorination of 2,4-dihydroxydiphenylethane according to the method used for the corresponding methane derivative. It crystallizes in needles melting at 136.7° (uncorr.); yield, 40%.

Anal. Subs., 5.637 mg.: AgCl, 3.331 mg. Calcd. for $C_{14}H_{13}O_2Cl$: Cl, 14.25. Found: Cl, 14.62.

Preparation of **5-Bromo-2,4-dihydroxydiphenylmethane, $C_6H_2(OH)_2BrCH_2C_6H_5$.**—The bromination was carried out in exactly the same way as the chlorination, using the theoretical quantity of bromine. The same method of purification was used. The compound melts at 122.4' (uncorr.); yield, 71%.

Anal. Subs., 15.329 mg.: AgBr, 10.415 mg. Calcd. for $C_{13}H_{11}O_2Br$: Br. 28.67. Found: Br, 28.92.

Preparation of 5-Bromo-2,4-dihydroxydiphenylethane, $C_6H_2(OH)_2BrCH_2CH_2$-C_6H_5.—This compound was prepared exactly like the foregoing one from 2,4-dihydroxydiphenylethane. It melts at 152.1° (uncorr.).

Anal. Subs.. 14.774 mg.: AgBr, 9.408 mg. Calcd. for $C_{14}H_{13}O_2Br$: Br, 27.27. Found: Br, 27.10.

B. Bacteriological

The determination of the phenol coefficients was carried out according to a modified Rideal-Walker procedure, using 0.5 cc. of broth culture to 5 cc. of diluted disinfectant. The dilutions of disinfectant were prepared in such a way that first the solid substance was dissolved in a small quantity of alcohol and then diluted with water. In no case was the concentration of alcohol more than 5% at the final dilution when the killing of the germ took place. The organic matter used in the investigation of the impairment of germicidal efficacy was a solution of 5% gelatin (French Gold Label) and 10% peptone "Difco." One cc. of this solution was added to 4 cc. of the dilute disinfectant, so that the final solution before introduction of the culture contained 1% of gelatin and 2% of peptone. Subcultures were made after five, ten and fifteen minutes of contact of bacteria and disinfectant, one loop being transplanted into fresh media.

Our thanks are due to Dr. V. A. Shternov and Mr. A. Grawehr for the determination of the phenol coefficients.

Summary

It appears from previous experiments that certain aryl derivatives of resorcinol show a very pronounced germicidal action. Since it is known that halogenation leads to derivatives, the germicidal efficacy of which is more pronounced than that of the unsubstituted compounds, we were interested in determining the influence of the introduction of chlorine and bromine into 2,4-dihydroxydiphenylmethane and -ethane (benzyl- and phenylethylresorcinol). Another point studied was the difference resulting from the introduction of the halogen into the unsubstituted or the dihydroxyl substituted nucleus. It has been found that halogenation greatly increases the germicidal efficacy of these compounds against B. *typhosus* and *Staph. pyog. aureus.* Some interesting observations have been made regarding reduction of the germicidal efficacy of these substances by "organic matter." The methods of preparation of the new compounds 4′-chloro- and 4-bromo-2,4-dihydroxydiphenylmethane and 5-chloro- and 5-bromo-2,4-dihydroxydiphenylmethane and -ethane have been described.

BLOOMFIELD, NEW JERSEY

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXI. COMPARISON OF TENDENCIES OF SATURATED AND UNSATURATED ALDEHYDES TOWARD CYCLIC ACETAL FORMATION

BY HAROLD HIBBERT, EDWARD O. HOUGHTON[1] AND K. AUSTIN TAYLOR[2]

RECEIVED NOVEMBER 8, 1928 PUBLISHED FEBRUARY 5, 1929

Previous work on cyclic acetal formation carried out during the last few years[3] has dealt only with the cyclic acetals from saturated carbonyl derivatives. The tendency of unsaturated aldehydes toward cyclic acetal formation has apparently not been investigated.

The possibility that the lignin complex, as it occurs in wood, may contain an unsaturated aldehyde grouping,[4] and that in this case the latter may be linked up with a carbohydrate complex in the form of a cyclic acetal, or half acetal, pointed to the necessity for obtaining further information regarding the interaction of unsaturated aldehydes with polyhydroxy compounds.

In the present investigation experiments were carried out on the condensation of ethylene glycol with cinnamic aldehyde, α-monochlorocinnamic aldehyde, β-phenyl-α,β-dichloropropionaldehyde, a-methyl-@-ethylacrolein, crotonaldehyde, α-monochlorocrotonaldehyde and dichlorobutyraldehyde, using dilute sulfuric or phosphoric acid as catalyst.[5] The yields of cyclic acetal obtained provide a basis for comparison of the tendencies of saturated and unsaturated acetals toward cyclic acetal formation.

The unsaturated cinnamic and crotonaldehydes and a-methyl @-ethylacrolein, show practically no tendency to form cyclic acetals under the given experimental conditions, the yields obtained being almost negligible. In the case of cinnamic and crotonaldehydes, the yield of the cyclic acetals was not sufficiently high to enable them to be separated and identified as such. With α-methyl-β-ethyl-acrolein a yield of about 10% of an impure product was obtained, the analysis of which corresponded approximately to that of the acetal.

The unsaturated halogenated aldehydes, containing chlorine attached to the a-carbon atom, show a greater tendency toward cyclic acetal for-

---

Holder of Bursary, Canadian National Research Council.

[2] Holder of Abitibi Power and Paper Company Research Fellowship.

The authors wish to express their thanks to the Canadian National Research Council, the Abitibi Power and Paper Company and the Canadian Pulp and Paper Association for the generous support accorded them.

[3] Hibbert and co-workers, J. Ind. *Eng. Chem.*, 13,256,334 (1921); THIS JOURNAL 45,734,2433, 3108,3117,3124 (1923); 46, 1283 (1924); 50, 1411,2235, 2242 (1928).

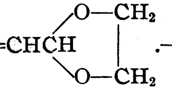
[4] Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926, pp. 277–285.

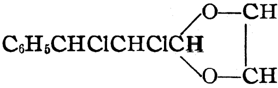
[5] Five-tenths to 1 cc. of the 40% acid was employed per mole of aldehyde used.

mation, apparently due to the activating influence exerted by the negative chlorine atom on the carbonyl group. Both α-monochlorocinnamic aldehyde and α-monochlorocrotonaldehyde, when condensed with ethylene glycol, gave a yield of 22% of the cyclic acetal.

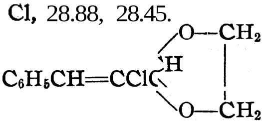
The saturated aldehydes, *viz*, phenyldichloropropionaldehyde and dichlorobutyraldehyde, readily formed cyclic acetals with yields of 37 and 50%, respectively.[6]

Experimental Part

Cinnamylidene Ethylene Glycol,  $C_6H_5CH{=}CHCH\left\langle\begin{array}{l}O-CH_2\\ \vert\\ O-CH_2\end{array}\right.$.—Thirty-three grams (one-quarter mole) of cinnamic aldehyde, thirty-one grams (one-half mole) of ethylene glycol and three drops of 40% sulfuric acid as catalyst were heated to 100° on the water-bath for six hours. The reaction mixture was then neutralized with solid potassium carbonate, extracted with ether and the ether extract dried and distilled. A small yield of the acetal was indicated but could not be separated from the large amount of unchanged aldehyde present.

β-Phenyl-α,β-dichloropropylidene Ethylene Glycol,  $C_6H_5CHClCHClCH\left\langle\begin{array}{l}O-CH_2\\ \vert\\ O-CH_2\end{array}\right.$.—β-Phenyldichloropropionaldehyde was prepared according to the method of Naar.[7] Two hundred and three grams (1 mole) of the aldehyde was condensed with 124 g. (2 moles) of ethylene glycol by heating at 70° for four hours. The hydrochloric acid split off from the aldehyde was sufficient to bring about the condensation. The ether extract was shaken with saturated sodium bisulfite solution to remove any unchanged aldehyde, washed, dried and the recovered oil distilled; b. p. 164–166° at 8 mm.; yield, 37%.

Anal. Calcd. for $C_{11}H_{12}O_2Cl_2$: Cl, 28.74. Found: Cl, 28.88, 28.45.

α-Monochlorocinnamylidene Ethylene Glycol,  $C_6H_5CH{=}CClC\begin{array}{l}\diagup O-CH_2\\ {}^{\diagdown}H \quad\ \vert\\ \diagdown O-CH_2\end{array}$.—α-Monochlorocinnamic aldehyde (b. p. 132–134° at 8 mm.) was prepared by a modification of Naar's method by refluxing β-phenyldichloropropionaldehyde with aqueous sodium acetate. One mole of the chloro-aldehyde and two moles of ethylene glycol were heated at 130° for three hours, using three drops of 40% sulfuric acid as catalyst. The mixture was extracted in the usual manner, yielding an opaque, reddish oil which

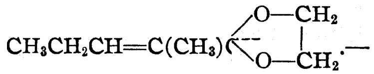
---

[6] From the recently published work of Adkins, This Journal, 49, 2517 (1927), relating to equilibrium data on simple acetal formation, it is apparent that the tendency of unsaturated aldehydes to form acetals is very much less pronounced than that of the saturated, a fact which seems to point to the much lower stability of the acetals from the former. Possibly by working in a medium of much lower acid concentration it might be possible to isolate the cyclic acetals from unsaturated aldehydes. Experiments are in progress using other condensing agents such as copper sulfate, calcium chloride, zinc chloride, iodine, etc.

[7] Naar, *Ber.*, 24, 244 (1891). A more convenient method of preparing the dichloro-aldehyde is to dissolve the theoretical amount of chlorine in carbon tetrachloride and to add this to the cinnamic aldehyde at −5°; yield, 72%; b. p. 94–97° (2 mm.).

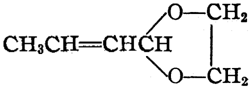
on cooling deposited the acetal in the form of fine, white crystals. These were recrystallized from benzene; m. p. 69–70'; yield, 22%. The crystals were readily soluble in alcohol, ether and benzene.

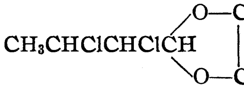
Anal. Subs.: 0.2110, 0.2017; CO_2, 0.4867, 0.4646; H_2O, 0.1023, 0.0960. Calcd. for $C_{11}H_{11}O_2Cl$: C, 62.70; H, 5.23; Cl, 16.86. Found: C, 62.90, 62.82; H, 5.38, 5.28; Cl, 17.72, 17.60.

α-Methyl-β-ethylacrylidene Ethylene Glycol, 
$CH_3CH_2CH{=}C(CH_3)C\left<\begin{array}{l}O{-}CH_2\\ \quad\;\,|\\ O{-}CH_2\end{array}\right.$.—

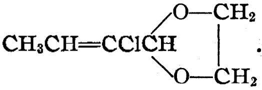
Twenty grams of **α-methyl-β-ethyl-acrolein,** condensed in a similar manner with 25 g. of ethylene glycol, using three drops of 40% sulfuric acid as catalyst, gave a high-boiling fraction, b. p. 170–174° (12 mm.), which was free from aldehyde (semicarbazide reaction). This product is the acetal but is evidently contaminated with other products.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.60; H, 9.86. Found: C, 66.42, 66.74; H, 9.82, 9.55.

Crotylidene Ethylene Glycol, 
$CH_3CH{=}CHCH\left<\begin{array}{l}O{-}CH_2\\ \quad\;\,|\\ O{-}CH_2\end{array}\right.$.—One hundred and forty grams (two moles) of crotonaldehyde was heated with 186 g. (three moles) of glycol for four hours at 95°, using 2 cc. of 20% phosphoric acid as catalyst. Examination of the mixture showed that only a negligible amount of condensation had occurred.

Dichlorobutylidene Ethylene Glycol, 
$CH_3CHClCHClCH\left<\begin{array}{l}O{-}CH_2\\ \quad\;\,|\\ O{-}CH_2\end{array}\right.$.—Dichlorobutyraldehyde was prepared by passing the theoretical quantity of chlorine into crotonaldehyde at −5°. One hundred and forty-one grams (one mole) of the crude aldehyde was then condensed directly, without any further purification, with 91 g. (1.5 moles) of glycol by heating on the water-bath for one hour. No catalyst was added. The yield of acetal (b. p. 100–105°, 13–15 mm.) was 50.3%.

Anal. Calcd. for $C_6H_{10}O_2Cl_2$: Cl, 38.37. Found: Cl, 37.74.

a-Monochlorocrotylidene Ethylene Glycol, 
$CH_3CH{=}CClCH\left<\begin{array}{l}O{-}CH_2\\ \quad\;\,|\\ O{-}CH_2\end{array}\right.$.—α-Monochlorocrotonaldehyde (b. p. 147–150°, 760 mm.) was prepared by mixing dichlorobutyraldehyde with aqueous sodium acetate and steam distilling the product. Seventy grams (two-thirds mole) of the aldehyde was condensed with 62 g. (one mole) of glycol, using 1 cc. of 20% phosphoric acid as catalyst. Considerable polymerization occurred. After extraction, the acetal obtained was refractionated several times under reduced pressure; b. p. 76–80' (14 mm.); yield, 22%.

Anal. Calcd. for $C_6H_9O_2Cl$: Cl, 23.87. Found: Cl, 23.45, 23.58.

Summary

1. A comparison has been made of the tendency of saturated and unsaturated aldehydes to form cyclic acetals. The aldehydes were condensed with ethylene glycol, using dilute sulfuric or phosphoric acid as catalyst, and the yields of the resulting cyclic acetal determined.

2. The unsaturated aldehydes, cinnamic aldehyde, crotonaldehyde and

α-methyl-β-ethyl-acrolein show practically no tendency toward cyclic acetal formation under the experimental conditions used.

3. The unsaturated aldehydes containing chlorine attached to the α-carbon atom, namely, α-monochlorocinnamic aldehyde and α-monochlorocrotonaldehyde, give a yield of about 22% of the corresponding cyclic acetal. The greater tendency of these aldehydes to form cyclic acetals is probably due to the activating influence exerted by the negative chlorine atom on the carbonyl group.

4. The saturated aldehydes, *viz.*, phenyldichloropropionaldehyde and dichlorobutyraldehyde, show the normal tendency of saturated aldehydes to form cyclic acetals, the yields being 37 and 50%, respectively.

PULP AND PAPER RESEARCH INSTITUTE
MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

SYNTHESIS OF CYCLOBUTANE ACIDS. I. NORPINIC ACID

BY CARL A. KERR

RECEIVED DECEMBER 5, 1928 PUBLISHED FEBRUARY 5, 1929

It is remarkable that while *cis*-cyclobutane-1,3-dicarboxylic acid,[1] methylcyclobutane[2] and 1,2-dimethylcyclobutane-3,4-dicarboxylic acid[3] have been synthesized from open-chain compounds, all attempts to effect cyclobutane ring closure in carbon chains having the gem.-dimethyl group as substituent have failed. This is particularly evident from the repeated failures to synthesize the well-known norpinic acid or 2,2-dimethylcyclobutane-1,3-dicarboxylic acid, which is a key acid formed in the oxidation of α- and β-pinene and some other terpene compounds. In an attempt to synthesize norpinic acid, Ganguly[4] found that ethyl α,α′-dibromo-β,β-dimethylglutarate did not react with methylene iodide in the presence of sodium to give the expected cyclobutane compound, while Vogel[5] showed that the disodium derivative of ethyl-β,β-dimethyl-α-cyanopropane-α,α′,α′-tricarboxylate failed to give a ring compound when treated with methylene iodide. Clemo and Welch[6] failed to get a cyclic compound from an attempted condensation of maleic or fumaric ester and dimethylketene, and further showed that the disodium derivative of β,β-dimethylpropane-α,α,α′,α′-tetracarboxylic ester did not react with methylene iodide to give a cyclobutane compound, as expected. Prior to the publication of Clemo

---

[1] Bottomley and Perkin, *J. Chem. Soc.*, 77, 298 (1900); Simonsen, *ibid.*, 93, 1778 (1908).

[2] Perkin, *ibid.*, 53, 201 (1888).

[3] Vogel, *ibid.*, 129, 1986 (1927).

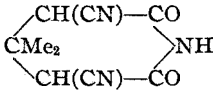
[4] Ganguly, *J. Ind. Inst. Science*, 5, 23 (1922).

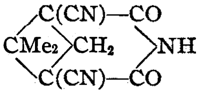
[5] Vogel, *J. Chem. Soc.*, 130, 2010 (1928).

[6] Clemo and Welch, *ibid.*, 130, 2621 (1928).

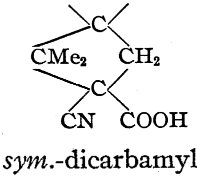
and Welch's experiments[6] the author had also failed to get ring closure between methylene iodide and the same disodium derivative used by these authors. In spite of the failure of Ganguly's experiment[4] with β,β-dimethyl-α,α-dibromoglutaric ester, it seemed probable that a,@,@-trimethyl-α,α'-dibromoglutaric ester, as a result of the position of its additional methyl group, might react with methylene iodide in the presence of sodium to give the ester of caryophyllenic acid or 2,2,1-trimethylcyclobutane-1,3-dicarboxylic ester, but the products of this reaction were unsaturated esters, with no evidence of ring formation.

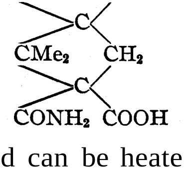
In view of these discouraging results with open-chain compounds, it was thought that if an easily ruptured six-membered ring were first formed, the spacial configuration of the atoms might be more prone to the formation of four-membered rings, and this proved to be the case. The six-membered ring chosen was Guareschi's[7] imide, α,α'-dicyano-β,β-dimethylglutarimide (I) and it was found that the sodium derivative of this compound reacted with methylene iodide to give a 70% yield of the dicyclic imide (II). It is interesting to note that in spite of the number of ways in which sodium derivatives of (I) might react with methylene iodide, cyclobutane ring formation took preference. The proof of the constitution of (II) was established by its hydrolysis to glutaric acid, by the formation of a mono-silver salt, and by determination of its molecular weight.


I


II

Hydrolysis of the dicyclic imide (II) by sulfuric acid at temperatures ranging from 80 to 140° ruptured the cyclobutane ring with the formation of varying quantities of glutaric acid and of phorone, which was undoubtedly formed from acetone produced by the disruption of the ring and the addition of water. Treatment of (II) with 100% phosphoric acid or with nitrous acid failed to produce a nitrogen-free acid. On the other hand, dilute alkali produced about equal quantities of *sym.*-dicyanonorpinic acid (III) and *sym.*-dicarbamylnorpinic acid (IV) when boiled with the imide.


III

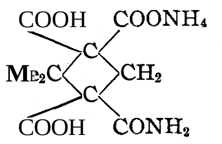

IV

Although *sym.*-dicarbamylnorpinic acid can be heated with four molecular equivalents of sodium hydroxide without hydrolysis taking place, both (III) and (IV) are hydrolyzed to the corresponding 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid (V) by concentrated alkali. A

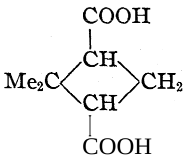
---

[7] Guareschi, *Atti, accad. sci. Torino,* 34,928 (1899).

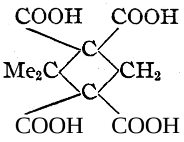
point of particular interest in regard to (IV) is the conversion of one of the carbamyl groupings to the corresponding ammonium salt by the addition of a molecule of water. Pure *sym.*-dicarbamylnorpinic acid, when dissolved in boiling water and the solution evaporated, leaves a white, crystalline water-soluble compound which has the structure represented by (VI).



VI



VII



V

An acidified aqueous solution of (VI) deposits crystals of a water-insoluble acid containing nitrogen, m. p. 236°, which gives 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid on boiling with concentrated alkali, and is probably 1-carbamyl-2,2-dimethylcyclobutane-1,3,3-tricarboxyic acid. This compound is still being studied with a view to proving its structure definitely.

When 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid (V) is heated at 200 to 205°, until no further evolution of carbon dioxide takes place, an oil remains which solidifies. This substance proved to be *trans*-norpinic acid (VII), described by Perkin and Simonsen,[8] who prepared it from the cis modification, which is an oxidation product of pinene. *Trans*-norpinic acid softened at 138° and melted at 146°, after repeated recrystallization from water. It is easily soluble in water, ether, alcohol and acetone, and separates in hard nodules from either aqueous solution or hydrochloric acid.

Now that a satisfactory method has been found for the formation of substituted cyclobutane acids in good yield, that is, by the condensation of substituted α,α′-dicyanoglutarimides with methylene iodide and hydrolysis of the resulting dicyclic compounds, the syntheses of other cyclobutane acids are under investigation, especially that of 2,2,1-trimethylcyclobutane-1,3-dicarboxylic acid, known as caryophyllenic acid and which is a key product in the oxidation of caryophyllene. Up to the present neither the structure of caryophyllenic acid nor of caryophyllene has been definitely determined.

Experimental

Ethyl **α,α′-Dibromo-α,β,β-trimethylglutarate.**—This was prepared by the method of Pandya and Thorpe.[9] Attempted condensation of the dibromo ester with methylene iodide in the presence of sodium failed, the product of the reaction being a mixture of unsaturated esters.

β,β-Dimethylpropane-α,α,α′,α′-tetracarboxylic Ester.—On preparing this ester

---

[8] Perkin and Simonsen, J. *Chem. Soc.*, 95, 1176 (1909).

[9] Pandya and Thorpe, *ibid.*, 123,2852 (1923).

according to the method of Kötz,[10] the high yields claimed by this author could not be attained. Using ether, benzene, toluene and methyl alcohol in turn as solvent, methylene iodide was allowed to react with the discdium derivative of β,β-dimethylpropane-$\alpha,\alpha,\alpha',\alpha'$-tetracarboxylic ester, but the product proved to be a mixture of malonic ester, *iso*propylidene malonic ester and a small undistillable residue.

β,β-Dimethyl-α,α'-dicyanoglutarimide was prepared according to the instructions of Kon and Thorpe,[11] but yields of only 60% of pure imide could be obtained, instead of 75%, as claimed by Kon and Thorpe.[11]

Condensation of **β,β-Dimethyl-α,α'-dicyanoglutarimide** with Methylene **Iodide.**—To a solution of 7.2 g. (6 atoms) of sodium in 100 cc. of methyl alcohol was added 20 g. of the imide and the whole refluxed on the steam-bath for one-half hour. Forty-four g. (3 moles) of methylene iodide was added through the condenser and refluxing continued for one and one-half hours, when all the methylene iodide had gone into solution. After standing overnight the mixture was again heated for one hour, cooled and the reaction mixture poured into 200 cc. of water containing 20 cc. of concd. nitric acid. Dicyanonorpinimide at once separated, was isolated by filtration and washed in the filter funnel several times with ether to remove the considerable quantity of methylene iodide which collects with the precipitate. When dried on a porous plate a yield of 15.5 g. was found and on recrystallization from glacial acetic acid 12 g. of pure dicyanonorpinimide separated in fine rhomboidal plates, m. p. 305–306° (decomp.). An attempt to purify dicyanonorpinimide by neutralizing with alkali and acidification by hydrochloric acid failed, only a small quantity of the imide being reprecipitated. Dicyanonorpinimide is slightly acid to litmus and is insoluble in all the common organic solvents and in water. It dissolves readily in alkali and in ammonium hydroxide.

Anal. Calcd. for $C_{10}H_9O_2N_3$: C, 59.1; H, 4.4; N, 20.7. Found: C, 58.5; H, 4.6; N, 20.4. Mol. *wt.* Calcd.: 203. Found: 203, 209.

Silver Salt of **Dicyanonorpinimide.**—When ammoniacal silver nitrate is added to a solution of the imide in ammonium hydroxide, the mono silver salt separates slowly.

Anal. Calcd. for $C_{10}H_8O_2N_3Ag$: Ag, 34.8. Found: Ag, 34.2.

Action of Sulfuric Acid on **Dicyanonorpinimide.**—3.6 g. of dicyanonorpinimide was added to 5.4 cc. of sulfuric acid and then 1 cc. of water. After heating on a sand-bath at 135° until all evolution of carbon dioxide had ceased, 1.8 cc. of water was added and heating continued at 140° for one hour. The cooled mixture was diluted with water and by extraction with ether six times an oil resulted which soon crystallized. This on recrystallization from hot benzene melted at 98–99° and was proved to be glutaric acid from a mixed melting point and analysis.

Anal. Calcd. for $C_5H_8O_4$: C, 45.5; H, 6.1. Found: C, 45.3; H, 6.3.

In the hope of obtaining norpinic acid, the imide was hydrolyzed as above by sulfuric acid, but the temperature was maintained at 100° throughout. Glutaric acid was again formed. At 80° sulfuric acid produces a very small yield of an acid containing nitrogen which was not identified. From the action of alkaline hydrogen peroxide on the imide no definite products could be isolated.

Preparation of *Sym.*-**dicyanonorpinic** Acid and *Sym.*-**dicarbamylnorpinic** Acid.—Dicyanonorpinimide on treatment with dilute alkali gives both *sym.*-dicyanonorpinic acid and *sym.*-dicarbamylnorpinic acid, the yield of the latter increasing with prolonged heating of the reaction mixture. The yellow solution obtained by dissolving 10 g. (1 mole) of dicyanonorpinimide in 180 cc. of 2.15% sodium hydroxide (slight excess over 2 moles) on heating gives off ammonia. At the end of two hours the solution was con-

---

[10] Kotz, J. *prakt. Chem.*, [2] 75,498 (1907).

[11] Kon and Thorpe, J. *Chem. Soc.*, 119,818 (1919).

centrated to half its bulk, acidified with sulfuric acid and 25 cc. of concentrated sodium sulfate solution was added. A white, crystalline solid separated from solution in flat plates, which when filtered, washed well with ice cold water and dried had a m. p. of 190° (decomp.). This was pure *sym.*-dicarbamylnorpinic acid; yield, 5.0 g.

Anal. Calcd. for $C_{10}H_{14}O_6N_2$: C, 46.5; H, 5.4; N, 10.85. Found: C, 46.8; H, 5.5; N, 10.75. Equivalent (by Ag salt method): 127.5. Calcd. equivalent: 129.

The acid filtrate above was extracted six times with ether and on concentrating the dried ethereal extracts a solid separated. This can be crystallized from glacial acetic acid but separates from this solvent with one molecule of acetic acid attached. It is best recrystallized from a mixture of ether and petroleum ether (40–60°) and separates in small, hard nodules, m. p. 225–226° (decomp.). This was *sym.*-dicyanonorpinic acid; yield, 4.0 g.

Anal. Calcd. for $C_{10}H_{10}O_4N_2$: C, 54.0; H, 4.5; N, 12.6. Found: C, 53.9; H, 4.6; N, 12.5. Calcd. equivalent, 111. Found: equivalent (from silver salt): 111.

The dimethyl ester of *sym.*-dicyanonorpinic acid can be prepared by refluxing the dried silver salt of the acid with excess of methyl iodide in ether solution for twelve hours. The ether solution on filtration and concentration gives the solid dimethyl ester, which may be purified by recrystallization from ether and separates in short prisms, m. p. 139–140°.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: C, 57.6; H, 5.6. Found: C, 57.8; H, 5.7.

Action of Water on *Sym.*-dicarbamylnorpinic Acid.—Although this substance is quite insoluble in cold water, it was found that it readily dissolves on heating, but the substance recovered by evaporation of the solvent was found to be a totally different compound, being soluble in water and chlorohydrin and giving off ammonia in the cold on grinding with sodium hydroxide, whereas the dicarbamylnorpinic acid has none of these properties. That one of the dicarbamyl groups passed over to the corresponding ammonium salt was shown by analysis of the compound and the existence of two equivalents.

Anal. Calcd. for $C_{10}H_{16}O_7N_2$: N, 10.15. Found: N, 10.21. Calcd. equivalent (by silver salt): 92; by titration with potash: 138. Found equivalent: 92; by titration with potash: 138.

On acidification of an aqueous solution of this mono-ammonium salt with dilute sulfuric acid, a precipitate of a water-insoluble acid comes down slowly. This acid is soluble in ether and, though not definitely identified, is most probably 1-carbamyl-2,2-dimethylcyclobutane-1,3,3-tricarboxylic acid, since it also gives 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid on further hydrolysis with concentrated alkali.

Preparation of 2,2-Dimethylcyclobutane-1,1,3,3-tetracarboxylic Acid.—When 0.75 g. (1 mole) of *sym.*-dicarbamylnorpinic acid was heated with 0.52 g. (4.5 moles) of sodium hydroxide under reflux for one and a half hours and then acidified, a precipitate at once was formed. This when washed well with water and dried had a melting point of 185–190° and was unchanged dicarbamylnorpinic acid; yield, 0.5 g. However, when 3.7 g. of *sym.*-dicarbamylnorpinic acid was refluxed with 50 cc. of 10% sodium hydroxide solution for nine hours, acidified with sulfuric acid and extracted five times with ether, an oil was found which slowly solidified. The solid was partially purified by filtering its aqueous solution and boiling down the filtrate to dryness. It can be purified by recrystallization from a mixture of acetone and benzene, being very soluble in the former. When pure, 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid melts at 200° and is very soluble in water, acetone and alcohol, but insoluble in benzene, chloroform and petroleum ether. The equivalent of this acid is difficult to determine, as a very indefinite end-point is experienced on direct titration with alkali and the silver salt tends to be explosive on heating. By mixing the silver salt with a little pure cane sugar before heating, an equivalent was found.

Anal. Calcd. for $C_{10}H_{12}O_8$: C, 46.15; H, 4.6. Found: C, 46.4; H, 4.7. Calcd. equivalent: 65. Found: 66.

Tetramethyl Ester of **2,2-Dimethylcyclobutane-1,1,3,3-tetracarboxylic** Acid.—This ester can be made by refluxing the silver salt of the acid with excess of methyl iodide in ether solution for twelve hours. The filtered ether solution gave an uncrystallizable oil which distilled with slight decomposition at 100° (25 mm.).

Anal. Calcd. for $C_{14}H_{20}O_8$: C, 53.1; H, 6.3. Found: C, 53.4; H, 6.4.

The Action of Alkali on *Sym.*-**dicyanonorpinic** Acid.—When heated for six hours under reflux a solution of 2.0 g. of dicyanonorpinic acid in 25 cc. of 20% caustic soda ceased to evolve ammonia. The mixture was acidified with sulfuric acid and extracted six times with ether; by concentrating the dried ether extracts an oil remained which solidified. This on purification gave a melting point of 200° and was proved to be 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid by a mixed melting-point determination; yield, 1.2 g.

Preparation of *Trans*-**norpinic** Acid.—When 3.5 g. of 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid was maintained at 200–205° for half an hour, all evolution of carbon dioxide ceased. On cooling, the dark yellow oil solidified. This was dissolved in water, filtered and concentrated to small bulk on the water-bath. Crystals which softened at 132° and melted at 140° separated, and these after two further recrystallizations from aqueous solution yielded a substance which softened at 138° and melted at 146°. This is without doubt trans-norpinic acid, described by Perkin and Simonsen,[8] who prepared it from cis-norpinic acid by heating with hydrochloric acid, and who record that it softens at 137 and melts at 144°. In agreement with Perkin and Simonsen it was found that trans-norpinic acid separates in hard nodules from concd. hydrochloric acid.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.8; H, 6.9. Found: C, 56.0; H, 6.9.

This opportunity is taken to express thanks to Professor M. Gomberg, who not only granted every facility for this research, but also gave the benefit of his very wide experience in the experimental problems which arose in this investigation. To the Commonwealth Fund the author is also indebted for a Fellowship during the tenure of which this work was carried out.

Summary

1. The syntheses of trans-norpinic acid, dicyanonorpinic acid, dicarbamylnorpinic acid and 2,2-dimethylcyclobutane-1,1,3,3-tetracarboxylic acid are described.

2. The synthesis of a new type of bicyclic imide, dicyanonorpinimide, is described.

3. A method capable of general application has been found for the synthesis of substituted cyclobutanedicarboxylic acids.

ANN ARBOR, MICHIGAN

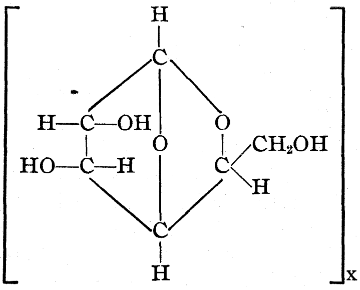
[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXII. THE ISOMERIC CINNAMYLIDENE GLYCEROLS

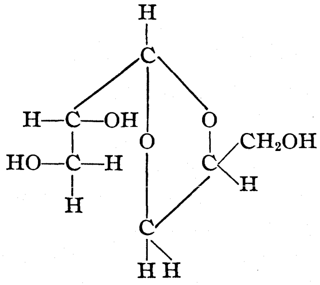
BY HAROLD HIBBERT AND MYRON S. WHELEN[1]

RECEIVED DECEMBER 18, 1928 PUBLISHED FEBRUARY 5, 1929

The properties of cyclic acetals and the nature of cyclic acetal formation in relation to carbohydrates and polysaccharides have been repeatedly emphasized in the course of this series of communications. Of added interest is the close connection for example, between cellulose, considered as an anhydro glucose (I) (a suggestion first put forward by one of us)[2] and 1,2-dihydroxypropylidene glycerol (II).[3]



I



II

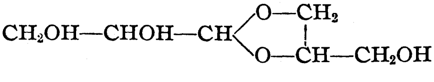
For this reason it becomes highly desirable to synthesize such derivatives as 1,2-dihydroxypropylidene glycerol (II) and glycol, in order to

---

[1] Holder of Studentship, Canadian National Research Council. The authors wish to express their thanks to the Canadian National Research Council and the Canadian Pulp and Paper Association for the generous support accorded to them.

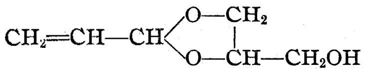
[2] Hibbert, *Chem. Met.* Eng., 22, 838 (1920). The constitution of cellulose was discussed at length in a later communication [Hibbert, *Ind.* Eng. *Chem.*, 13, 256, 334 (1921)] in which the view was taken that no decision could be reached as to whether this substance was to be regarded as a polymerized (or associated) anhydroglucose or as a very large ring compound. The question still remains an open one, as is evident from the recent discussions on this subject [Bergmann, Herzog and Jancke, *Naturwissenschaft.*, 16, 464 (1928); Kurt Hess and Carl Trogus, *Ber.*, 61, 1982 (1928); Meyer and Mark, *Ber.*, 61, 593 (1928)]; Kurt Meyer, Z. *ang. Chem.*, 41, 935 (1928); Sponsler and Dore, "Colloid Symposium Monograph," 4, 174 (1926); THIS JOURNAL, 50, 1940 (1928); Katz, "*Ergebn. exakt. Naturwiss.*" 3, 363, J. Springer, Berlin, (1924); 4, 185 (1928); Haworth, *Helv. Chim. Acta,* 11, 534 (1928). The extensive chemical investigations carried out by Kurt Hess in this field—an excellent summary of which is to be found in his recent valuable textbook on "Cellulose Chemistry"—provide, in the writers' opinion, considerable support for the theory that cellulose may be an associated form of an anhydro-dextrose building unit.

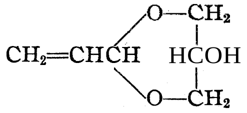
[3] The formula is more customarily written



$$CH_2OH—CHOH—CH\begin{matrix}/O—CH_2 \\ \quad | \\ \backslash O—CH—CH_2OH\end{matrix}$$

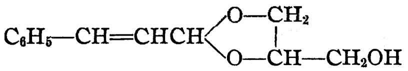
ascertain how far such structures exhibit a tendency toward polymerization or association.[4] The simplest mode of synthesis of these products appeared to lie in the primary preparation of cyclic acetals from unsaturated aldehydes (acrolein, trotonaldehyde, cinnamic aldehyde) and glycerol. Isolation of the two structurally isomeric acetals, for example (III) and (IV)

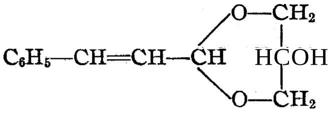

III


IV

could then be followed by conversion of (III) into the corresponding dihydroxy compound, *viz.*, dihydroxypropylidene glycerol (II).

Both acrolein and cinnamic aldehyde condense readily with glycerol, the former without the use of a catalyst. The present paper deals with the isolation, identification and properties of the two structurally isomeric cinnamylidene glycerols (V) and (VI).


V


VI

The only literature reference to cinnamylidene glycerol is a short communication by Peacock[6] in which he states this product may be "readily obtained as a viscous oil, which slowly solidifies to a mass of crystals, m. p. 110–112°," but gives no directions as to its preparation. He pointed out that the cinnamylidene group and the carbinol group may exhibit *cis-trans* isomerism with respect to the heterocyclic rings and that in addition to this possibility of isomerism there is also that due to the double linking in the cinnamylidene group, which may again cause the formation of *cis* and *trans* isomerides. The number of possible isomerides for each formula is therefore four, neglecting optically active members. Peacock only isolated a single isomer, the structure of which was left unsolved, and gave no indication of a belief in the possibility of *simultaneous* formation of both ring structures such as is demanded by the Michael partition principle.

Previous work carried out in this field[6] shows that in the condensation of a saturated aldehyde with glycerol, a partition between the 1,1′- and 1,2-hydroxyl groups always occurs, resulting in the formation of two structural ring isomers, *viz.*, a five- and a six-membered cyclic acetal, respectively. Peacock in his work apparently only expected to find a one-ring system. The simultaneous formation of both types is now shown to

---

[4] The synthesis of dihydroxypropylidene glycol has now been accomplished and that of dihydroxypropylidene glycerol is in progress.

[5] Peacock, *J. Chem. Soc.*, 107, 816 (1915).

[6] Hibbert and co-workers, THIS JOURNAL, 50, 2235, 2242 (1928).

be true in the cases of cinnamic aldehyde and the isolation and properties of two structural isomeric ethers (five- and six-membered ring isomers) of cinnamylidene glycerol are described in the experimental part. The process outlined serves as a convenient method for the synthesis of these somewhat inaccessible products.

In the condensation of cinnamic aldehyde and glycerol the crude cinnamylidene glycerol is left as a viscous oil which slowly solidifies in about twenty-four hours to a thick pasty mass of crystals, readily separable from the accompanying oil. Purification of the crystals, followed by methylation and hydrolysis, yields glycerol β-methyl ether, thus identifying the ring structure as the six-membered acetal (VI). The oil[7] remaining after the removal of the crystalline isomer and the unchanged cinnamic aldehyde, on similar treatment, yields glycerol a-methyl ether, thus serving to identify it as the five-membered acetal (V). It is of interest that the methyl ethers of both the 1,2- and 1,1′-cinnamylidene glycerols are very sensitive to hydrolysis (involving ring scission), much more so in fact than the free acetals. This is in agreement with observations made by Irvine, Macdonald and Soutar[8] on isopropylidene glycerol.

Only one of the numerous possible isomers of each of the structural five- and six-membered cinnamylidene glycerols was isolated, due possibly to the labile character of the other forms, although no special effort was made to investigate this phase of the problem, the direct object being to prove the simultaneous formation of both types of structural ring isomerism.

Investigations dealing with the action of benzoyl hydroperoxide on the cinnamylidene glycerols and the synthesis of phenyl 1,2-dihydroxypropylidene glycerol are in progress.

Experimental

Preparation **and** Isolation of the Isomeric **Cinnamylidene** Glycerols.--One hundred and thirty-two g. (1 mole) of pure cinnamic aldehyde, 92 **g.** of glycerol and five drops of 40% sulfuric acid were heated together with constant shaking by hand in a round-bottomed pyrex Bask under a pressure of 20 mm. At approximately 50° water began to distil over. At the same low pressure the temperature was gradually raised during the course of approximately twenty-five minutes to 100°, at which it was maintained for thirty minutes, or until there was complete miscibility and water ceased to be given off. The reaction product was a viscous oil which slowly solidified after about twenty-four hours to a **thick,** pasty mass of crystals, the pasty mass containing a considerable quantity of an adhering oil. This product was disintegrated and thoroughly washed with water at 30° to remove unchanged glycerol and sulfuric acid, then filtered and pressed as dry as possible on a suction filter, the solid remaining as a thick, pasty mass. This was dissolved in warm benzene, separated from water in a separatory funnel and the warm benzene solution dried by shaking with anhydrous sodium sulfate. On filtering the hot solution and cooling, yellowish-white crystals separated out which

---

[7] It was not found possible to isolate this product in a sufficiently pure state for analysis.

[8] Irvine, Macdonald and Soutar, J. Chem. *Soc.*, **107, 337 (1915).**

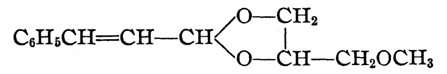
on recrystallization from benzene yielded **38** g. of long, asbestos-like needles, m. p. 121°.

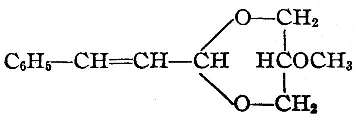
Anal. Subs., 0.1557: CO_2, 0.4004; H_2O, 0.090. Calcd. for $C_{12}H_{14}O_3$: *C*, 69.90; H, 6.79. Found: *C*, 70.08; *H*, 6.54. Molecular weight determinations carried out in ethylene bromide gave values ranging from 238–260; theoretical, 206.

Attempts to crystallize the unpurified oil obtained after the removal of the above solid were futile. Distillation under reduced pressure was unsatisfactory, yielding only a portion of unchanged cinnamic aldehyde and a small amount of oil, b. p. 200–225° (6 mm.), which solidified on cooling. This solid was identified as 1,1′-cinnamylidene glycerol which had not been removed by crystallization. The bulk of the mother liquor remained as a gummy product and, as shown later, consisted of the 1,2-cinnamylidene glycerol.[7]

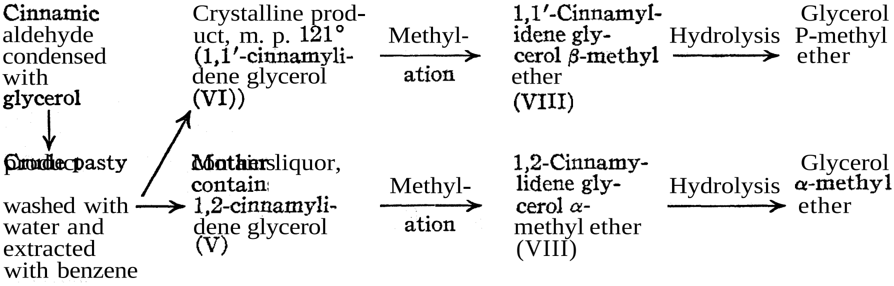
During the course of this investigation the very labile character of these carbon–oxygen cyclic structures was observed, in that samples of the solid 1,1-cinnamylidene glycerol, m. p. 121°, slowly changed on standing into an oily liquid. From analogy with the corresponding benzylidene glycerols[9] this was presumably due to an interconversion of one isomeric form into the other, but the product was not investigated.

Determination of Structure.—The methylation hydrolysis method of Irvine and co-workers was followed in order to determine the identification of the isomeric cinnamylidene glycerols. Methylation with silver oxide and methyl iodide gave the corresponding cinnamylidene glycerol methyl ethers (VII) and (VIII)


VII


VIII

the crystalline 1,1′-cinnamylidene glycerol (VI) (m. p. 121°) giving exclusively the crystalline 1,1′-cinnamylidene glycerol β-methyl ether (VIII), and the mother liquor from the original condensation reaction, after removal of the acetal (VI) yielding the liquid 1,2-cinnamylidene glycerol a-methyl ether (VII). Hydrolysis of the latter product gave glycerol a-methyl ether, while hydrolysis of the former yielded glycerol β-methyl ether as indicated in the following scheme



---

[9] Hill, Whelen and Hibbert, THIS JOURNAL, 50,2235 (1928).

No trace of the crystalline β-methyl ether (VIII) was found in the methylation product obtained from the liquid acetal (V) although it is admittedly impossible to remove all of the solid acetal (VI) from the liquid acetal (V) by crystallization.

Synthesis of 1,1'-Cinnamylidene Glycerol β-Methyl Ether (VIII).—Thirty-three grams of crystalline 1,1'-cinnamylidene glycerol (VI) was methylated in the usual manner, using 60 g. of silver oxide and 115 g. of methyl iodide. The reaction mixture was thoroughly extracted with warm benzene from which, on partial evaporation and cooling, 1,1'-cinnamylidene glycerol β-methyl ether (VIII) separated, mixed with a small amount of unchanged 1,1'-cinnamylidene glycerol. Fractional recrystallization from benzene, with final recrystallization from ligroin (b. p. 80–90°), yielded 13 g. of white, pearly leaflets, m. p. 79–80°. The only other substance isolated was 4.8 g. of white needles, m. p. 115–118°. A mixed melting point determination with approximately equal quantities of this substance and 1,1'-cinnamylidene glycerol (m. p. 121°) gave a m. p. of 119°, showing these substances to be identical.

Anal. (1,1'-Cinnamylidene Glycerol β-Methyl Ether.) Subs., 0.1596 : CO_2, 0.4180; H_2O, 0.970. Calcd. for $C_{13}H_{16}O_3$: C, 70.86; H, 7.33. Found: C, 71.43; H, 6.80.

Hydrolysis of 1,1-Cinnamylidene Glycerol β-Methyl Ether (VIII).—Sixteen g. of crystalline cinnamylidene glycerol β-methyl ether was hydrolyzed by boiling under a reflux condenser for seventy minutes with 150 cc. of 75% aqueous ethyl alcohol containing 0.5% of hydrochloric acid. Fifty cc. of water was then added and the alcohol removed under reduced pressure.

The considerable quantity of cinnamic aldehyde present was separated in a separatory funnel from the hydrolysis product and the latter extracted with ether. The aqueous solution was then neutralized with lead carbonate, filtered and concentrated under reduced pressure. The residual oil on distillation yielded 3.8 g. of glycerol β-methyl ether, b. p. 123" (13 mm.); $n_D^{17°}$, 1.4497.[8]

Anal. Subs., 0.1345: CO_2, 0.2208; H_2O, 0.1119. Calcd. for $C_4H_{10}O_3$: C, 45.28; H, 9.45. Found: C, 44.78; H, 9.26.

Methylation of 1,2-Cinnamylidene Glycerol.—The benzene solution obtained after removal of the crystalline 1,1'-cinnamylidene glycerol (p. 623) was concentrated in order to remove the solvent and thirty grams of the residual mother liquor containing the 1,2-cinnamylidene glycerol was then methylated in the usual manner with 60 g. of silver oxide and 115 g. of methyl iodide. The reaction mixture was extracted with benzene, the solvent evaporated and the residual oil fractionated. It yielded 9.4 g. of cinnamic aldehyde and 13.2 g. of 1,2-cinnamylidene glycerol a-methyl ether, b. p. 164–166° (6 mm.); $n_D^{20°}$, 1.5455.

Attempts to obtain a satisfactory analysis were unsuccessful due to the ease of hydrolysis and difficulties in combustion of the material. As in cated below, however, its identity was definitely established by its hydrolysis into glycerol a-methyl ether.

Hydrolysis of Cinnamylidene Glycerol a-Methyl Ether.—Twelve g. of cinnamylidene glycerol methyl ether, on hydrolysis by the same method as used for the @-derivative, yielded 3.6 g. of glycerol a-methyl ether, b. p., 110" (13 mm.); $n_D^{17°}$, 1.4435.

Anal. Subs., 0.1588: CO_2, 0.2609; H_2O, 0.1291. Calcd. for $C_4H_{10}O_3$: C, 45.23; H, 9.45. Found: C, 44.80; H, 9.09.

Ease of Hydrolysis of the Cinnamylidene Glycerols and Ethers.—When compared with the methylidene and benzylidene glycerols and their corresponding ethers, the cinnamylidene glycerol derivatives exhibit a very much more pronounced tendency toward hydrolysis.

Summary

1. Cinnamic aldehyde when heated with glycerol and a small amount of 40% sulfuric acid under reduced pressure readily condenses to give a pasty crystalline mixture of isomeric five- and six-membered cinnarnylidene glycerols.

2. From the crude material a crystalline solid and an oil can be readily separated, the former of which is shown to be the six-membered acetal (1,1′-cinnamylidene glycerol) and the latter the five-membered derivative (1,2-cinnamylidene glycerol).

PULP AND PAPER RESEARCH INSTITUTE
McGILL UNIVERSITY, MONTREAL, CANADA

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

OMEGA-HYDROXY ALIPHATIC ACIDS. SYNTHESIS OF SABINIC ACID

BY W. H. LYCAN[1] AND ROGER ADAMS

RECEIVED DECEMBER 27, 1928 PUBLISHED FEBRUARY 5, 1929

In a previous research[2] it was shown that the ethyl esters of w-aldehydo aliphatic acids could be prepared readily by the ozonization of various unsaturated esters. These substances are convenient intermediates for the preparation of the esters of w-hydroxy aliphatic acids, since the aldehyde esters are quantitatively converted by means of hydrogen and platinum to the corresponding alcohols. By saponification the ω-hydroxy acids result. In this investigation the five compounds, 9-hydroxynonanoic, 10-hydroxydecanoic, 11-hydroxyundecanoic, 12-hydroxydodecanoic and 13-hydroxytridecanoic acids have been synthesized and studied.

$$\left.\begin{array}{l} CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \\ CH_2{=}CH(CH_2)_8CO_2CH_3 \\ CH_2{=}CH(CH_2)_9CO_2CH_3 \\ CH_2{=}CH(CH_2)_{10}CO_2CH_3 \\ CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2CH_3 \end{array}\right\} \xrightarrow{O_3} CHO(CH_2)_xCO_2CH_3 \xrightarrow{2H} CH_2OH(CH_2)_xCO_2CH_3 \longrightarrow CH_2OH(CH_2)_xCO_2H$$

The o-hydroxy acids are of interest from several standpoints: first, a number of them are naturally occurring compounds; second, they may be valuable intermediates for the synthesis of large-membered lactones and, third, they offer an opportunity to study the compounds formed by intermolecular esterification.

Among such acids isolated from natural sources which have been studied

---

[1] This paper is an abstract of a thesis submitted by W. H. Lycan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Noller and Adams, THIS JOURNAL, 48, 1074 (1926); Tomecko and Adams, *ibid.*, 49, 920 (1927); Davies and Adams, *ibid.*, 50, 1749 (1928).

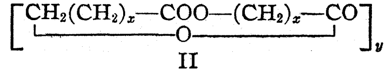
are sabinic and juniperic acids. These were extracted by Bougault[3] and the structures determined as 12-hydroxydodecanoic acid and 16-hydroxyhexadecanoic acid, respectively. The synthetic 12-hydroxydodecanoic acid, which melted at 83–84°, proved to be identical with the natural product, as determined by the melting point and mixed melting point with a sample of sabinic acid kindly furnished by Dr. Bougault. In a recent article by Bhattacharya, Saletore and Simonsen,[4] 12-hydroxydodecanoic acid was prepared as an intermediate in the course of another investigation. It was reported as melting at 78–79°. The method of synthesis might readily lead to the presence of impurities difficult to remove and the low melting point indicates this to be the case. During the preparation of this manuscript, a paper by Ruzicka and Stoll[5] has come to hand which describes ω-hydroxy acids containing 13 to 17 carbon atoms. The method of preparation used by them differed entirely from that used in this research and consisted in the saponification of the corresponding lactones produced in turn by the oxidation of the cyclic ketones. It was found that the 16-hydroxyhexadecanoic acid was identical with juniperic acid. Moreover, the melting point of the 13-hydroxytridecanoic acid proved to be identical with that obtained for the same acid in this investigation.

Large-membered lactone rings have been shown to occur naturally by Kerschbaum[6] who isolated the lactone of ambrettolic acid and of pentadecanolic acid from certain natural oils. Such ring compounds are also of considerable importance from a purely theoretical standpoint as they offer an opportunity to study quantitatively the relative stability of large rings. In the latest paper by Ruzicka,[5] our work along this line has been anticipated. He has prepared analogous large-membered lactones by oxidizing the corresponding cyclic ketones.

The study in this Laboratory is, therefore, being centered on the preparation of intermolecular esters from the hydroxy acids. These compounds, possible structures for which are represented by Formulas I and II, present an interesting field of polymeric-like substances which, on account of their properties, may readily be studied.

$HO—[(CH_2)_x—COO—(CH_2)_x]_y—COOH$ or

I



$$\left[\underset{\llcorner\text{———————O———————}\lrcorner}{CH_2(CH_2)_x—COO—(CH_2)_x—CO}\right]_y$$

II

Bougault[3] believed that sabinic and juniperic acids probably existed in the plant in the form of such polymers which he designated as etholides.

---

[3] Bougault and Bourdier, *Compt. rend.*, 147, 1311 (1908); *J. pharm. chim.*, [6] 29, 561 (1909); [6] 30, 10 (1909); Bougault, *Compt. rend.*, 150, 874 (1910); *J. pharm. chim.*, [7] 1, 425 (1910); 3, 101 (1911); Bougault and Cattelain, *Compt. rend.*, 186, 1746 (1928).

[4] Bhattacharya, Saletore and Simonsen, *J. Chem. Soc.*, 2678 (1928).

[5] Ruzicka and Stoll, *Helv. Chim. Acta*, 11, 1159 (1928).

[6] Kerschbaum, *Ber.*, 60, 902 (1927); German Patent application 105,677.

Ruzicka[6] noticed by-products in the oxidation of the cyclic ketones which he assumed to be etholides. One of these he purified and by analysis showed it to be a dimolecular compound. In this investigation the 9-hydroxynonanoic acid was heated and converted into a well-crystallized polymer melting at 64–66°, which analyzed also for a dimolecular compound. It has not yet been determined whether the molecule consists of a simple dimolecular lactone, a polymer of such a lactone or a very long, open-chain compound in which the free hydroxyl and carboxyl groups have practically no effect on the analysis. It is readily saponified by aqueous potassium hydroxide to the simple hydroxy acid. A more quantitative study of these substances and their derivatives will be reported in a subsequent paper.

Experimental Part

Methyl Esters of ω-Aldehydo Aliphatic Acids.—The method of preparation of the methyl esters of the ω-aldehydo acids and the unsaturated esters from which they are made has been described in previous papers.[2] The ozonizations of the methyl esters of 11,12-dodecenoic acid and 12,13-tridecenoic acid have not been as fully described as those of the other unsaturated acids used in these syntheses. In this communication are described the by-products obtained in the two ozonizations mentioned, the monomethyl esters of nonane-1,9-dicarboxylic acid and decane-1,10-dicarboxylic acid, respectively, isolated from the residues remaining after the distillation of the corresponding aldehyde esters.

Monomethyl Ester of Decane-1,10-dicarboxylic Acid.—The residue from the distillation of ω-aldehydo-undecanoate was recrystallized six times from petroleum ether (b. p. 50–60°) and melted at 51.5–52°.

Anal. Subs., 0.1784: CO_2, 0.4692; H_2O, 0.1953. Calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.91. Found: C, 63.73; H, 9.94.

Nonane-1,9-dicarboxylic acid, m. p. 109–110°, and decane-1,10-dicarboxylic acid, m. p. 126.5–127°, were obtained by the hydrolysis of the monomethyl esters with 10% aqueous sodium hydroxide solution and subsequent acidification.

Semicarbazone of Methyl 11-Aldehydo-undecanoate.—The semicarbazone was prepared by shaking equal weights of the aldehyde ester and semicarbazide sulfate with twice the weight of sodium acetate in dilute alcohol solution. The semicarbazone was recrystallized several times from ethyl acetate; m. p. 90–92°.

Anal. Subs., 0.1659: CO_2, 0.4179; H_2O, 0.1953. Calcd. for $C_{14}H_{28}O_3N_3$: C, 58.70; H, 9.84. Found: C, 58.36; H, 9.50.

Methyl Esters of the ω-Hydroxy Aliphatic Acids.—The methyl esters of the ω-aldehydo acids were reduced to the corresponding methyl esters of the ω-hydroxy acids according to the method of Carothers and Adams[7] for the reduction of aldehydes to primary alcohols. A solution of 0.2 mole of the aldehyde ester in 100 cc. of 95% ethyl alcohol, to which had been added 0.2 g. of platinum oxide catalyst and 2 cc. of freshly prepared 0.1 M ferrous sulfate solution, was shaken with hydrogen under about 2.5–3 atm. pressure. Usually about two hours were required for the absorption of the theoretical quantity of hydrogen. The solution was then filtered to remove the platinum black and the alcohol was removed on a steam-bath. The hydroxy ester was dissolved in 350 cc. of ether and the ether solution was washed, first with 150 cc. of 20% sodium

---

[7] Carothers and Adams, THIS JOURNAL, 45, 1071 (1923).

bisulfite solution, then with **150** cc. of **10%** sodium carbonate solution and finally with **500 cc.** of water. The ether solution was then dried with anhydrous magnesium sulfate. The alcohol esters were finally distilled under diminished pressure. The yields were from **80–90%** of the theoretical.

TABLE I

METHYL ESTERS OF ω-HYDROXY ACIDS

	Unsaturated ester	ω-Hydroxy ester	B. p., °C. (3 mm.)	M. p., °C.	n_D	d^{20}
1	Methyl oleate	$CH_2OH(CH_2)_7CO_2CH_3$	137–139	.....	1.4438	0.9588
2	Methyl undecenoate	$CH_2OH(CH_2)_8CO_2CH_3$	145–147	.....	1.4471	.9618
3	Methyl dodecenoate	$CH_2OH(CH_2)_9CO_2CH_3$	156–159	.....	1.4493	,9542
4	Methyl tridecenoate	$CH_2OH(CH_2)_{10}CO_2CH_3$	164–166	34–35	....	....
5	Methyl erucate	$CH_2OH(CH_2)_{11}CO_2CH_3$	170–173	40.5–41.5	....	....

ANALYSES

	Subs.. g.	CO_2, g.	H_2O, g.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	0.2270	0.5337	0.2204	63.80	10.71	64.20	10.86
2	.1792	.4255	.1746	65.28	10.96	64.76	10.89
3	.1969	.4788	.1934	66.60	11.19	66.32	10.97
4	.1825	.4517	.1875	67.76	11.38	67.50	11.44
5	.2000	.4796	.1908	68.85	11.56	68.55	11.67

Phenyl Urethans of the Methyl Esters of the **ω-Hydroxy Acids.**—The phenyl urethans of the methyl esters of the w-hydroxy acids were prepared by mixing the ester with one-third its weight of phenyl isocyanate. The reaction was ordinarily spontaneous and was hastened by gentle warming on a hot-plate. The mixture was allowed to stand for one hour, after which the product was purified by repeated. crystallizations from petroleum ether or mixtures of benzene and petroleum ether (b. p. 50–60°).

TABLE II

PHENYL URETHANS OF THE METHYL ESTERS OF ω-HYDROXY ACIDS

	Formula	M. p., °C. (corr.)	Analyses Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_6H_5NHCO_2(CH_2)_8CO_2CH_3$	53–54	66.40	8.20	66.15	8.42
2	$C_6H_5NHCO_2(CH_2)_9CO_2CH_3$	54–55	67.24	8.47	67.08	8.50
3	$C_6H_5NHCO_2(CH_2)_{10}CO_2CH_3$	64.5–65.5	68.01	8.72	68.14	8.81
4	$C_6H_5NHCO_2(CH_2)_{11}CO_2CH_3$	64–65	68.76	8.95	68.54	8.79
5	$C_6H_5NHCO_2(CH_2)_{12}CO_2CH_3$	73.5–74	69.45	9.16	69.34	9.24

ω-Hydroxy Aliphatic Acids.—The methyl esters of the w-hydroxy acids were hydrolyzed with a 10% excess of **10%** aqueous potassium hydroxide solution. The hydrolysis of **0.1** mole of the ester required about two and one-half hours. When solution was complete the water was removed by evaporation on the steam-bath and the potassium salts thus obtained were crystallized three times from absolute ethyl alcohol. The potassium salts crystallized as fluffy white crystals which analyzed for the theoretical percentage of potassium. The pure salt was dissolved in a small amount of water and evaporated on a steam-bath to remove traces of alcohol. It was again dissolved in water and the acid was freed by titration to Congo Red paper with **1** N hydrogen chloride solution. The acid which separated as a gelatinous precipitate was extracted with ether, the ether solution washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under diminished pressure at ordinary temperatures and the resulting acids were purified by careful crystallization.

The compounds were dissolved in hot ethyl acetate and immediately cooled in an ice-and salt-bath. Crystallization in the usual way resulted in the formation of a small amount of insoluble polymeric material.

TABLE III

ω-HYDROXY ACIDS

	Formula	M. p., °C. (corr.)	Analyses Calcd., % C	H	Found, % C	H
1	$CH_2OH(CH_2)_7CO_2H$	53–54	62.07	10.43	62.30	10.67
2	$CH_2OH(CH_2)_8CO_2H$	75–76	63.77	10.72	63.56	10.75
3	$CH_2OH(CH_2)_9CO_2H$	65.5–66	65.29	10.96	65.36	10.83
4	$CH_2OH(CH_2)_{10}CO_2H$	83–84	66.59	11.20	65.50	11.20
5	$CH_2OH(CH_2)_{11}CO_2H$	77–78	67.82	11.39	67.88	11.39

Polymer of 9-Hydroxynonanoic Acid.—When 9-hydroxynonanoic acid was heated at a pressure of 3 mm. for half an hour at 220–230°, water was eliminated and a polymer-like product was obtained. This substance was crystallized from a mixture of benzene and petroleum ether (b. p. 50–60°) and was obtained as a fluffy, white, finely-divided powder; m. p. 64–66°.

Anal. Subs., 0.1921, 0.1898; CO_2, 0.4852, 0.4793; H_2O, 0.1774, 0.1765. Calcd. for $(C_9H_{16}O_2)_x$: **C,** 69.18; **H,** 10.33. Found: C, 68.88, 68.86; H, 10.33, 10.40.

This compound was insoluble in the cold in ethyl alcohol, petroleum ether, acetone and ethyl acetate, but was soluble in the hot. It was insoluble in cold aqueous potassium hydroxide solution. Upon warming with 10% aqueous potassium hydroxide solution on a steam-bath for one hour hydrolysis was complete. The potassium salt was crystallized from absolute alcohol and the acid freed as before was identical with the 9-hydroxynonanoic acid.

Molecular weight determinations in benzene both by boiling-point and freezing-point methods gave such variable results that more reliable data are needed before publication.

Summary

1. A general method is given for the preparation of w-hydroxy esters and w-hydroxy acids by reduction of the aldehydo esters obtained upon ozonization of the methyl esters of unsaturated acids.
2. A polymer of one of these w-hydroxy acids is described.

URBANA, ILLINOIS

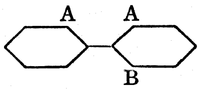
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

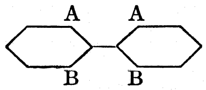
STEREOISOMERISM OF DIPHENYL COMPOUNDS. RESOLUTION OF 3,3'-DIAMINODIMESITYL. II[1]

BY WENDELL W. MOYER[2] AND ROGER ADAMS

RECEIVED JANUARY 17, 1929 PUBLISHED FEBRUARY 5, 1929

The diphenyl compounds which have thus far been resolved into pairs of mirror images have, in every case, been 2,6,2'-trisubstituted, or 2,6,-2',6'-tetrasubstituted compounds, represented by the two general formulas I and II.


I


II

Of Type I only compounds in which A = carboxyl, B = nitro[3] have been made; of Type II, several combinations have been prepared in which A = carboxyl, B = nitro;[4] A = carboxyl, B = chlorine;[5] A = carboxyl, B = methoxyl;[6] A = amino, B = methyl;? A = acetamino, B = methyl;? A = acetamino, B = carboxyl;[7] A = carboxyl, B = the —CH= group in a benzene nucleus;[8] A = carboxyl, B = —CO— group in an anthraquinone nucleus.[9] It is thus reasonably certain that there is no specific effect due to any particular group.

Owing chiefly to experimental difficulties, other diphenyl derivatives with three or four substitutions in the 2,6- and 2,'6'-positions of the general tri- and tetrasubstituted type A,B,C, or A,B,C,D, have not been prepared and studied, but it can hardly be questioned that these could also exist in the form of optical isomers.

The only reasonably logical explanation of such isomerism is to assume that the two benzene rings are coaxial and not coplanar. The important problem then resolves itself into determining the mechanism by which various groups located in the 2,6- and 2',6'-positions as outlined above can prevent free rotation of the nuclei.

Turner and Le Fèvre[10] suggested that the electrical nature of the sub-

---

For previous papers see Hyde and Adams, THIS JOURNAL, 50,2499 (1928).

[2] This communication is an abstract of a portion of a thesis submitted by Wendell W. Moyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Christie and Kenner, J. *Chem. Soc.*, 123, 779 (1923); *ibid.*, 470 (1926); Christie, Holderness and Kenner, *ibid.*, 671 (1926).

[4] Christie and Kenner, ibid., 121, 614 (1922).

[5] Christie, James and Kenner, *ibid.*, 123, 1948 (1923).

[6] Kenner and Turner, ibid., 2340 (1928).

[7] Meisenheimer and Höring, *Ber.*, 60, 1425 (1927).

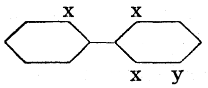
[8] Kiihn and Albrecht, Ann., 464, 91 (1928).

[9] Kiihn and Albrecht, ibid., 465, 282 (1928).

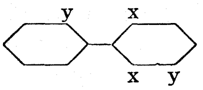
[10] Turner and Le Fèvre, J. *Soc. Chem. Ind.*, 45, 831 (1926); ibid., 45,883 (1926).

stituted groups, the residual affinity on each ring and the internuclear forces were important influences. They believe the isomerism arises from an inherent property of the parent hydrocarbon. Such a theory would lead to the expectation of easy racemization in optically active diphenyl compounds. Bell and Kenyon[11] preferred to look on the isomerism as due, primarily, to the ortho-substituting groups acting as obstacles to free rotation, though they believed the size and electrical character of the substituting groups might have an influence. On the other hand, Mills[12] considered the isomerism to be entirely mechanical in character. He assumed that the 2,6- and 2′,6′-groups are unable to get by each other due to their size and their proximity in space, and thus the two rings are never in the same plane.

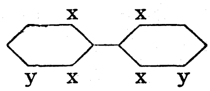
In a previous paper[1] it was pointed out that on the basis of the mechanical theory three other types of diphenyl compounds should be capable of resolution, Formulas III, IV and V.



III

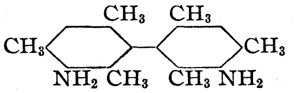


IV

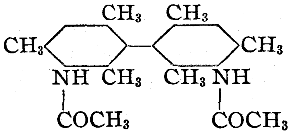


V

Here the substituting groups in the 2,6- and 2′,6′-positions are the same and the individual rings are asymmetric, due to the substitution of some group in the proper position. In this investigation two compounds have been made which fall into the class represented by Formula V. The substances are 3,3′-diaminodimesityl (VI) and 3,3′-diacetaminodimesityl (VII).



VI



VII

The 3,3′-diaminodimesityl was readily resolved into its optical isomers. The d- and l-forms were both isolated pure; d = $[\alpha]_D + 42.3°$, $l = [\alpha]_D$ $-41.5°$, and from them the active diacetaminodimesityls were prepared. The d-diaminodimesityl was boiled for long periods with both alcoholic potassium hydroxide and hydrochloric acid. No racemization took place with the alkali and only an extremely slight change in the rotation was noted with the acid treatment.

The fact that groups in the 2,6- and 2′,6′-positions in resolvable diphenyls may be the same, and that the compounds are not easily racemized, eliminates the possibility of explaining the isomerism as being caused entirely by the electrochemical character of the ortho substituted group. The presence of the two amino or acetamino groups produces

---

[11] Bell and Kenyon, *J. Soc. Chem.* Ind., 45, 864 (1926).

[12] Mills, *ibid.*, 45,884 (1926).

asymmetry in each of the rings, a condition which must be fulfilled if optical isomerism is to be possible, even though the rings are not in the same plane. These results offer strong additional evidence that the present mechanical theory may be correct.

To prepare diaminodimesityl, monobromomesitylene was converted to the Grignard, which by the action of cupric chloride gave, in better than 20% yields, dimesityl. This procedure is far more satisfactory than that described in the literature, the action of copper on mono-iodomesitylene. Considerable difficulty was encountered in the nitration of dimesityl, since all of the common nitrating reagents gave either a pure tetranitro derivative or a mixture of mono, di and tri. Acetyl nitrate proved satisfactory, however, and yielded a pure dinitro compound, even though an excess of reagent was used. Since by the use of this reagent mesitylene can be nitrated only to the mono nitro derivative, it seems certain that the dinitrodimesityl must be the 3,3′-substitution product. The reduction to the corresponding diamino was carried out in the usual way and the resolution of the latter was very readily accomplished through the dicamphorsulfonate. There was an extremely wide variation in the solubility of the diastereoisomeric salts and as a consequence the isolation of both forms in a pure state was a simple matter. The salts, on hydrolysis, gave the pure "d" and "*l*" bases. The active diacetamino derivatives were made by the action of acetic anhydride on the active diamino dimesityls.

It might be stated that attempts to condense nitro-iodomesitylene with copper to get the same dinitrodimesityl mentioned above were unsuccessful. Moreover, several experiments attempting the partial reduction of tetranitrodimesityl to 3,3′-dinitro-5,5′-diaminodimesityl resulted in mixtures. There was no difficulty in preparing 3,3′-dibromodimesityl but attempts to form the corresponding mono Grignard and from it the carboxylic acid gave negative results.

The facts that compounds of this type may be resolved and, moreover, that they may readily be prepared, make possible a much wider study of this general field. Other tetra-ortho-substituted compounds of a similar character are now being prepared. Compounds containing a di-ortho-substituted benzene nucleus attached to another residue, not a benzene, in which the atom combined to the benzene may have a fixed structure, are also being studied.

Experimental Part

Preparation of Dimesityl.—The application of the general method for preparing hydrocarbons discovered by Sakellarios and Kyrimis[13] was found much more satisfactory for preparing dimesityl than the method described by Ullmann.[14]

---

[13] Sakellarios and Kyrimis, *Ber.*, **57**, 322 (1924).

[14] Ullmann, *Ann.*, **332**, 48 (1904).

In a 3-liter, three-necked flask fitted with a vigorous stirrer, reflux condenser and a 500-cc. dropping funnel were placed 48.7 g. of magnesium turnings and 125 g. of bromomesitylene in 150 g. of anhydrous ether, and a few crystals of iodine. By warming, without stirring, the reaction was started and allowed to proceed for a few minutes. Mechanical stirring was begun and a solution of 273 g. of bromomesitylene in 600 g. of dry ether was added at such a rate that the ether refluxed steadily. The addition of the halide required two and one-half to three hours, after which the solution was stirred for half an hour longer. The flask was then surrounded by ice and a suspension of 300 g. of finely powdered anhydrous cupric chloride in 600 cc. of dry ether was added as rapidly as the heating of the reaction mixture permitted. The flask was then warmed on a steam-cone until the ether refluxed gently and the stirring was continued for six hours. At the end of this time the mixture was cooled and poured slowly, with constant stirring, into cracked ice and strong hydrochloric acid. After the decomposition was complete, more hydrochloric acid was added in order to take all the cuprous chloride into solution. The ether layer was washed successively with hydrochloric acid, water, ammonia and water. After removing the ether, about 180 g. of low-boiling material distilled over and then 65 g. of dimesityl from 142–160° at 5 mm. The distillate solidified and upon crystallization from alcohol, 52 g. (22%) of dimesityl that melted at 99.5–100° was obtained.

Tetranitrodimesityl.—In small amounts at a time, 18 g. of dimesityl was added to 130 g. of fuming nitric acid (sp. gr. 1.50) which was stirred mechanically and cooled by a freezing mixture. When the dimesityl came in contact with the nitric acid, a dark coloration appeared for an instant and then quickly faded. Toward the end of the reaction some solid nitro compound separated from solution. The sides of the flask were washed down by 20 g. more of nitric acid and then, after standing for half an hour, the mixture was poured into cracked ice. The tetranitro compound separated as a slightly yellowish, flocculent precipitate which, after washing and drying, weighed 31.6 g. (quantitative yield). After recrystallization from glacial acetic acid, the compound was obtained pure and melted at 270–271°.

Anal. Subs., 0.2184: CO_2, 0.4146; H_2O, 0.0839. Calcd. for $C_{18}H_{18}O_8N_4$: C, 51.65; H, 4.34. Found: C, 51.77; H, 4.30.

Partial Reduction of **Tetranitrodimesityl.**—An attempt was made to reduce tetranitrodimesityl by means of alcoholic ammonium sulfide to 3,3′-diamino-5,5′-dinitrodimesityl in somewhat the same way that dinitromesitylene was reduced to nitro-aminomesitylene.

In the first attempt, 8 g. of tetranitrodimesityl was added to a solution of 18 g. of ammonium hydroxide (sp. gr. 0.90) in 55 g. of absolute alcohol that had been saturated with hydrogen sulfide gas. The mixture was placed in an autoclave and heated at 140–150° for twelve hours. The brownish-red reaction mixture was acidified with dilute hydrochloric acid, the sulfur filtered off and the alcohol distilled from the acid solution. Upon adding ammonia, a reddish-yellow precipitate came down. This product was recrystallized from dilute alcohol and obviously was a mixture. An analysis showed that the tetranitro compound had been reduced on the average just beyond the triamino stage.

A second reduction using 10 g. of tetranitrodimesityl with 10 g. of ammonium hydroxide in 35 g. of absolute alcohol saturated with hydrogen sulfide, at 105–110° for twelve hours, also gave a mixture.

3,3′-Dibromodimesityl.—To a solution of 6.37 g. of dimesityl in 20 g. of carbon tetrachloride was added, with stirring and cooling in ice-water, a solution of 8.6 g. of bromine in 10 g. of carbon tetrachloride. The solution was allowed to stand in the dark overnight, after which the carbon tetrachloride was removed under reduced pressure.

A solution of 2 g. of sodium in 50 cc. of 95% alcohol was then added to the residue and the solution refluxed for half an hour. The mixture was poured into water and the product extracted with ether. The compound (6.6 g. or 63%) obtained was recrystallized from alcohol several times. When pure it melted at 112–113°.

Anal. Subs., 0.3160: CO_2, 0.6369; H_2O, 0.1443. Calcd. for $C_{18}H_{20}Br_2$: C, 54.55; H, 5.09. Found: C, 54.97; H, 5.11.

An attempt to make a mono Grignard in ether solution was not very successful. Only part of the magnesium went into solution. When all evidences of reaction were over, carbon dioxide was introduced just over the surface of the solution. Upon working up in the usual way a gummy product resulted from which no pure substance could be separated.

Tetra-aminodimesityl.—Six grams of the mixture of aminonitrodimesityls, obtained by the partial reduction of the tetranitrodimesityl, was reduced in a similar manner to that used in the preparation of diaminodimesityl. The tetra-amino compound thus obtained was slightly colored, and this color was removed by treating with 150 cc. of boiling alcohol, in which the amine was insoluble, and then adding a slight excess of concentrated hydrochloric acid which took all of the material into solution. Upon cooling the hydrochloride separated in glistening yellowish crystals. The hydrochloride was dissolved in water and the tetra-aminodimesityl precipitated by ammonia as a white, finely-divided material. Upon standing in the light, the compound became colored to a yellow-brown. The crude product (3.5 g.) was recrystallized from dilute pyridine and gave buff-yellow crystals that did not melt at 360°.

3,3′-Dinitrodimesityl.—Acetyl nitrate was found to nitrate mesitylene to give a quantitative yield of pure mononitromesitylene and consequently was used as a reagent for the preparation of 3,3′-dinitrodimesityl. Acetyl nitrate is much more easily prepared than benzoyl nitrate, a reagent which had been shown by Francis[15] to react with mesitylene to give mononitromesitylene.

The acetyl nitrate was prepared according to the original method devised by Pictet and Khotinsky.[16] It was used in acetic anhydride solution (approximately 1 g. of nitrogen pentoxide in 3–4 g. of acetic anhydride). The molar concentration per gram of the solution used was calculated so that it was easy to weigh out definite amounts of the acetyl nitrate. The acetyl nitrate solution was kept at −15°; at room temperature it turns brown and evolves red fumes.

A solution of 0.1 mole (23.8 g.) of dimesityl was made in 70 g. of carbon tetrachloride and cooled to 0° with a freezing mixture. Then with mechanical stirring and continued cooling, an amount of the acetyl nitrate solution that contained 0.3 mole of acetyl nitrate was slowly added. Care must be taken to add only a few cc. until the reaction starts. After a few minutes considerable heat was evolved and the mixture warmed to 35–40°. The remainder of the acetyl nitrate was then added at such a rate that the temperature remained at this upper limit. In trial runs it was demonstrated that it was necessary to have a temperature of 30–40° (as high as 50° without harm) toward the end of the nitration until completion in order to obtain the dinitro derivative pure—if nitration continued throughout at 0–10°, a low-melting product was obtained (m. p. 100–109°) that was probably the mononitro derivative or a mixture of dinitro- and mononitrodimesityl.

After the heat of the reaction had ceased, the stirring was continued at room temperature for another hour. The mixture was decomposed with water and the carbon tetrachloride steam-distilled out. The dinitrodimesityl was filtered off as a granular

---

[15] Francis, Ber., **39**, 3801 (1906).

[16] Pictet and Khotinsky, *ibid.*, 40, 1163 (1907); *Compt.* rend., 144, 210 (1907).

mass and weighed **32** g. **(98%).** Alternate recrystallizations from acetic acid and alcohol gave a pure product of constant melting point, 162.5–163.5° (corr.).

Anal. **Subs., 0.2149: CO_2, 0.5193; H_2O, 0.1156. Calcd.** for $C_{18}H_{20}O_4N_2$: C, **65.82; H, 6.14.** Found: **C, 65.90; H, 6.02.**

Nitration of dimesityl in hot glacial acetic acid solution or in the cold with carbon tetrachloride as solvent and the theoretical amount of nitric acid gave mixtures of nitro products. Nitration with the theoretical amount (for the dinitro derivative) of potassium nitrate in concentrated sulfuric acid gave a mixture from which the tetranitro derivative was isolated.

3,3′-Diaminodimesityl.—To a solution of **180** g. of glacial acetic acid, 40 *g*. of water and **10 cc.** of concentrated hydrochloric acid, was added **16.4** g. of pure dinitrodimesityl. Then with constant stirring, **100** g. of zinc dust was added in small amounts. The flask was at first cooled in an ice mixture and the zinc added so that the temperature went to 80–90°. This temperature was maintained by the heat of reaction as long as possible; then it was allowed to cool as the reaction ceased. More water was added from time to time. Zinc acetate separated after two hours and the reaction was stopped. The mixture was filtered and the residue washed with water and dilute hydrochloric acid. The filtrate was then made alkaline with an excess of ammonia in order to take all of the zinc salts into solution. The flaky white diaminodimesityl was filtered and again treated with acid and ammonia in order to remove any traces of zinc salts. The dried product weighed **13.2** g. Several recrystallizations from **60%** alcohol raised the melting point to the constant value, 206–207° (corr.). The yield of pure diaminodimesityl was **8.2** g. **(61%).**

Anal. Subs., **0.1989: CO_2, 0.5880; H_2O, 0.1587.** Calcd. for $C_{18}H_{24}N_2$: **C, 80.53; H, 9.02.** Found: **C, 80.62; H, 8.93.**

3,3′-Diacetylaminodimesityl.—A mixture of **10** g. of acetic anhydride and **1** g. of pure diaminodimesityl was shaken for a few seconds. The diamino compound went into solution at once with evolution of heat, and then within two minutes the diacetyl derivative crystallized out from the anhydride solution. After standing for half an hour the compound was filtered and then washed thoroughly with water. The yield was quantitative and the derivative pure, as recrystallization from dilute methyl alcohol did not raise the melting point. **303–304'.**

Anal. Subs., **0.1656: CO_2, 0.4563; H_2O, 0.1212.** Calcd. for $C_{22}H_{28}O_2N_2$: C, **74.95; H, 8.01.** Found: C, **75.15;** H, **8.18.**

Resolution **of 3,3′-Diaminodimesityl.**—To 200 cc. of boiling water containing **9.8** g. (0.042 mole) of d-camphorsulfonic acid was added **5.36** g. (0.02 mole) of diaminodimesityl. When complete solution was effected, Norite decolorizing charcoal was added and the solution filtered. The filtrate was allowed to stand in a cool place for thirty-six hours. At the end of this time a crop of large, light-yellow, transparent crystals had separated, which were essentially a pure salt, as shown by rotation and melting point as compared with recrystallized material. These crystals were filtered from the solution and washed with cold water; weight, 6.5 g. The salt did not have a sharp melting point, 175–187°, and gradually softened with gas evolution. The compound was found to be hydrated and, after drying, melted at 186–188° with previous softening.

Rotation. **0.2020 g.** made up to **20 cc.** with water at **20°** gave $\alpha_D = +0.33°$, $l = 2$; $[\alpha]_D^{20} = +16.3°$.

The salt was recrystallized from **150 cc. of** water. The melting point again was not sharp, but it melted exactly like the original material.

Rotation. *(a)* **0.2170** g. made **up** to **20** cc. with water at 20° gave a, = +0.35°, I = 2; $[\alpha]_D^{20}$ = +16.1°. (b) **0.2265 g.** made up to **20** cc. with 95% alcohol at 20° gave α_D = +0.73°, l = 2; $[\alpha]_D^{20}$ = +32.2°.

The salt was again crystallized from water. The melting point did not change.

Rotation. **0.2255** g. made up to **20** cc. with 95% alcohol at 20° gave a, = +0.73°, l = 2; $[\alpha]_D^{20}$ = +32.4°.

Anal. (Parr Bomb). Subs., **0.5000: $BaSO_4$, 0.3056.** Calcd. for $C_{38}H_{56}O_8N_2S_2 \cdot H_2O$: S, 8.54. Found: **S, 8.40.**

Anal. Subs., **0.2434** g. (air-dried salt): 140–150° for three hours lost **0.0054** g. Calcd. for $C_{38}H_{56}O_8N_2S_2 \cdot H_2O$: **$H_2O$, 2.40.** Found: **$H_2O$, 2.22.**

The mother liquor from the first crystallization, to which none of the subsequent recrystallization filtrates had been added, was then evaporated to 80 cc. and allowed to stand in the cold for a week. At the end of this time 0.4 g. of salt was removed and the liquid was further concentrated to 25 cc. Upon standing for another week a small amount of finely granular material separated. The weight was 0.2 g., m. p. 174–189' with no gas evolution. The rotation in alcohol was +25.9° This was probably an impure sample of the more insoluble salt. The filtrate was shown to be a solution of the other diastereoisomeric salt in essentially pure form. No attempt was made to isolate the solid salt, but the solution was hydrolyzed directly to obtain the pure 1-base.

d-3,3′-**Diaminodimesityl.**—The pure crystalline (less soluble) dicamphorsulfonate salt was dissolved in an excess of hot water and the active diamino compound precipitated in white flakes with ammonia. After washing and drying, the compound was essentially pure, melting point 203.5–204.5 (corr.). Recrystallization from dilute alcohol did not raise the melting point and the product tended to acquire a slightly yellowish color.

Rotation. **(a)** 0 **1907** g. made up to **20** cc. with **0.3** N hydrochloric acid at 20° gave α_D = +0.23°, l = 2; $[\alpha]_D^{20}$ = +12.0°. (b) **0.2456** g. made up to **20** cc. with acetone at 20° gave α_D = +1.04°, l = 2; $[\alpha]_D^{20}$ = +42.3°.

d-**3,3′-Diacetaminodimesityl.**—The diacetyl derivative of the d-base was prepared in the same way as the racemic diacetate. The melting point of the compound, purified by crystallization from dilute alcohol, was 312–313° (corr.), with shrinking at 307°.

Rotation. **0.2370** g. made up to **20** cc. with absolute alcohol at 20° gave α_D = +0.73°, *1* = 2; $[\alpha]_D^{20}$ = +30.8°.

Anal. Subs., **0.1727: CO_2, 0.4738; H_2O, 0.1254.** Calcd. for $C_{22}H_{28}O_2N_2$: C, **74.95;** H, 8.01. Found: C, 74.82; H, 8.12.

1-3,3′-**Diaminodimesityl.**—The final mother liquors from the resolution were diluted to 100 cc. and the diamino precipitated with ammonia. After recrystallization from dilute methyl alcohol, it melted at 203–204° (corr.).

Rotation. **0.2265** g. made up to **20** cc. with acetone at 20° gave α_D = −0.94°, 1 = 2; $[\alpha]_D^{20}$ = −41.5'.

l-3,3′-Diacetaminodimesityl.—This derivative was made by the same method as described for the d-form. It melted at 311–313° (corr.), with previous shrinking at 307°.

Rotation. 0.2300 g. made up to 20 cc. with absolute alcohol gave $\alpha_D = -0.70'$. $l = 2$; $[\alpha]^{20}_{D} = -30.4°$.

Racemization Experiments.—The optical stability of the d-3,3′-diaminodimesityl was studied under two different sets of conditions.

1. A solution of 0.3 g. of the d-base in a mixture of 20 cc. of absolute alcohol and 3 g. of potassium hydroxide in 3 cc. of water was refluxed for five hours. The rotation of the recovered diamine showed that practically no racemization had occurred.

Rotation. 0.2262 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = +0.92°$, $1 = 2$; $[\alpha]^{20}_{D} = +40.7°$.

2. A solution of 0.2 g. of d-diaminodimesityl in 30 cc. of concentrated hydrochloric acid was refluxed for nine hours. Racemization took place to a very slight extent.

Rotation. 0.1645 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = +0.64$, $l = 2$; $[\alpha]^{20}_{D} = +38.9°$.

Nitro-aminomesitylene.—Dinitromesitylene was prepared by the action of cold fuming nitric acid on mesitylene at 0°, according to the method by Fittig.[17]

The partial reduction of dinitromesitylene to nitro-aminomesitylene was most readily accomplished by a modification of the original procedure of Kiister and Stallberg.[18] A solution of 100 g. of aqueous ammonia (sp. gr. 0.90) in 300 g. of absolute alcohol was cooled in an ice-bath and saturated with hydrogen sulfide. The ammonium sulfide solution was then placed in an autoclave with 80 g. of dinitromesitylene and the mixture heated at a temperature of 110–115" for fifteen hours. The yield (89%) was better than that reported previously.

Nitro-iodomesitylene.—To a hot solution of 150 cc. of water, 70 cc. of concentrated hydrochloric acid, and 5 cc. of alcohol, was added 27 g. (0.15 mole) of nitro-aminomesitylene and the solution cooled to 0°. As the solution cooled, the hydrochloride separated. To the cold mixture was then added with constant stirring, 10.5 g. of sodium nitrite in 20 cc. of water. The diazonium salt solution was filtered from insoluble material. Then with stirring a solution of 30 g. of potassium iodide in 50 cc. of water was added. A red solid separated and then as the mixture approached room temperature, nitrogen was evolved and the color changed to yellow. The mixture was warmed to 45° and allowed to stand for several hours. The product was filtered and treated with hot sodium hydroxide solution

---

[17] Fittig, Ann., 141, 133 (1867).

[18] Kiister and Stallberg, *ibid.*, 278, 213 (1894).

and acid successively. After recrystallization from alcohol a yield of 32.5 g. (72%) of buff-colored crystals was obtained, melting at 96–97°.

Anal. Subs., 0.2230: CO_2, 0.3133; H_2O, 0.0715. Calcd. for $C_9H_{10}O_2NI$: C, 37.11; H, 3.46. Found: C, 38.31; H, 3.59.

Several attempts to make 3,3′-dinitrodimesityl by the action of Naturkupfer C on nitro-iodomesitylene between temperatures of 200–300° gave only tars from which no definite compound was obtained. An attempt with nitrobenzene as a solvent yielded no better results.

Summary

1. 3,3′-Diaminodimesityl has been prepared and resolved through the dicamphorsulfonate to yield pure *l*- and d-modifications.
2. The active diamines were converted into the corresponding active diacetamino derivatives.
3. These are the first diphenyl derivatives resolved with the 2,6,2′,6′-positions, all occupied by the same group. This lends support to the mechanical theory for explaining the optical isomerism in certain diphenyl compounds.

URBANA, ILLINOIS

NOTE

The Electrolysis of Metallo-Organic Compounds.[1]—Gaddum and French[2] have recently reported a series of experiments on the electrolysis of ether solutions of the Grignard reagent. In their paper they comment on the chemical reactivity of the metallic magnesium which was deposited at the cathode but do not describe its physical properties. Some time ago the authors made a series of experiments on the electrolysis of magnesium ethyl bromide in ether solutions, using platinum electrodes. The solutions showed a good conductivity and a beautiful crystalline deposit of metallic magnesium quickly formed upon the platinum cathode. This deposit adhered quite firmly to the electrode surface. Products were detected in the solution similar to those reported by Gaddum and French, which are to be attributed to the anode reaction, but it is impossible to say whether these were produced by direct electrolysis or by a secondary reaction of bromine, which had been liberated at the anode, with the Grignard reagent. In order to get away from the effects of the halogen liberated at the anode, zinc diethyl was used in place of the Grignard reagents in some of the electrolysis experiments. Zinc diethyl in the pure state shows no appreciable conductivity but an ether solution showed a specific conductivity of 10^{-4}. With an applied potential of 110 volts

---

[1] The experimental results noted here were originally included in a paper which was submitted to THIS JOURNAL for publication in June, 1926.

[2] Gaddum and French, THIS JOURNAL, 49, 1295 (1927).

appreciable quantities of metallic zinc were deposited upon the cathode. The zinc deposit was smooth, firmly adherent and not of as brilliant a luster as the magnesium deposits obtained in the earlier experiments. The products at the anode dissolved in the solution and were not satisfactorily identified but there can be little doubt that the ethyl radical was liberated at the anode.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

WORTH H. RODEBUSH
J. MERRIAM PETERSON

RECEIVED OCTOBER 29, 1928
PUBLISHED FEBRUARY 5, 1929

NEW BOOKS

The Collected Works of J. Willard Gibbs, Ph.D., LL.D. Formerly Professor of Mathematical Physics in Yale University. Edited by WILLIAM RAYMOND LONGLEY and RALPH GIBBS VAN NAME. Two volumes. Longmans, Green and *Co.*, 55 Fifth Avenue, New York, N. Y., 1928. xxviii + 434 pp. xviii + 284 pp. 15.5 × 23.5 cm. Price, $6.00 per set.

This is the first complete edition of the writings of J. Willard Gibbs. It is a reprint of the 1906 publication, with the addition of "The Elementary Principles of Statistical Mechanics." The first volume contains the various contributions to thermodynamics, while the second comprises Statistical Mechanics, Dynamics, Vector Analysis and Multiple Algebra, Electromagnetic Theory of Light and some shorter papers, including a biographical sketch of Clausius and of H. A. Newton.

When the 1906 edition appeared, a very eulogistic foreign review expressed regret that the price of the volumes was so high; it was felt that the University or the Nation whose privilege it was to claim Gibbs as their own should have offered the world this fundamental contribution to science at a nominal price, "as a duty of honour." This reproach is now removed by the publication of the present collection at a price which "has been made possible by the generosity of Professor Irving Fisher of Yale University, a former pupil of Willard Gibbs, and by the economy resulting from the use of photographic reproduction, which was also desirable as a means of avoiding typographical errors."

It is now fifty years since the last of the articles on the "Equilibrium of Heterogeneous Substances" was published in the Transactions of the Connecticut Academy. The reviewer cannot help wondering how many books on thermodynamics written at the present day will bear republishing fifty years hence, without apology, without adaptation and without a single verbal change. Gibbs' thermodynamics has not been changed by other writers during this period, but the attitude of chemists has been changed profoundly. The durability characteristic of Gibbs' work is due to the complete absence of all matter extraneous to thermodynamics, which is nowadays often slipped in unawares or unannounced. The change in the public has been brought about by the very thing Gibbs so deliberately avoided, for the great number of less durable, but also less difficult, books which have been published since have had the very useful effect of popularizing thermodynamics, and the time is now ripe for a return to the master. The reviewer's advice to any chemists who may have, long ago, given up Gibbs in despair, is: Try him again, he's much easier than he used to be.

FRANK B. KENRICK

Kurzes Lehrbuch der Chemie in Natur und Wirtschaft. (A Short Treatise on Chemistry in Nature and Human Affairs.) Band I. Allgemeine Chemie. (Vol. I. General Chemistry.) By PROF. JOHANN MATULA; Anorganische Chemie. (Inorganic Chemistry.) Band II. Organische Chemie. (Vol. II. Organic Chemistry.) By PROF. CARL OPPENHEIMER. Second revised edition. Georg Thieme, Antonstrasse 15–19, Leipzig C 1, Germany, 1928. xvi + 566 pp. 65 figs. xiv + 471 pp. 7 figs. 17 X 24.5 cm. Price, Vol. I, unbound, M. 23; bound, M. 26; Vol. II, unbound, M. 19; bound, M. 22.

In the introduction to the first edition Professor Oppenheimer stated that this book arose from a desire to prepare a readable treatise of moderate length which should present the leading ideas on which chemistry has been developed into an unusually attractive and well ordered science, and which should also show the innumerable interrelations between chemistry and the work of the biologist and technologist. To this end the treatise was to contain everything that would serve to give a clear and adequate picture of the science, but in the choice of illustrative material preference was always to be given to matters that were important in nature, in the biological sciences or in industry. No substance was to appear in it unless it represented a type, was a natural product, had biological significance or technological interest. In the main, the authors have consistently followed this prescription.

Approximately half of the first volume is devoted to "general chemistry." This part, which was prepared by Professor Matula of Vienna, necessarily deals with many subjects that are usually treated in texts on physical chemistry, but the matter is presented as a necessary introduction to inorganic and organic chemistry—not as an independent discipline. Subjects like catalysis, complex formation, constitutional formulas, isomerism, tautomerism and polymerism, therefore, receive far more attention than they commonly do in books on physical chemistry. Professor Matula has a rare ability to present and apply physico-chemical principles without an elaborate use of mathematics, hence this section is exceptionally interesting and instructive for readers not primarily interested in physical chemistry.

In the remainder of the volume the senior author presents descriptive inorganic chemistry, interspersed with brief historical notes, discussions and practical applications. The descriptive material differs but little from that contained in other texts on the subject except in its very extensive use of structural formulas. These are written without evidence and with a finality that frequently is unwarranted. The historical notes **and** theoretical discussions also present little that is novel in content or treatment. But the author writes with real enthusiasm when he is dealing with topics of biochemical interest—the mechanism of biological oxidations, the fixation of nitrogen, the pharmacology of carbon monoxide, the role of iron compounds in living organisms and similar topics.

As will be seen from the foregoing description this treatise is in no sense a "popular" presentation; it presupposes at least as much knowledge as could be obtained in good fundamental courses in organic and inorganic chemistry. It should appeal especially to the biologist and the medical practitioner but it also contains much that is stimulating and extremely interesting to the chemist.

E. P. KOHLER

Atlas der letzten Linien der wichtigsten Elemente. (Atlas of the Persistent Lines of the Most Important Elements.) By DR. FRITZ LÖWE. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1928. iii + 44 pp. 13 plates. 15 X 22.5 cm. Price, bound, R. M. 12.

The chief value of this atlas for the spectrum analyst lies in the reproductions of spectra and the tables which it contains.

For 42 of the elements (chiefly metallic) reproductions of spectrograms with a wave-length scale are accompanied by lists of the wave lengths of the most important lines with their relative intensities in spark and arc. The spectra in each case cover the particular region of the ultraviolet where the most important lines occur. Condensed spark spectra with self-induction on lamp graphite are used. For each element the four spectra result from moistening the electrode with solutions of 1.0, 0.1, 0.01 and 0.001 normal concentration.

Following the plates is a wave-length table of persistent lines (656), according to de Gramont, and Pollok and Leonard, for 64 elements, with relative intensities in arc and spark, ionization state and wave length of the strong line of next longer wave length as given by Kayser. The range 1863–6708 Å. is covered.

References to more important literature are given.

G. P. BAXTER

Atomstruktur und Atombindung. (Valence and Atomic Structure.) By DR. J. STARK. Polytechnische Buchhandlung, A. Seydel, Koniggratzerstrasse 31, Berlin, S. W. 11, Germany, 1928. xx + 198 pp. 15 figs. 14.5 X 22.5 cm. Price, R. M. 9.

In this book the author presents at considerable length a theory of atomic and molecular structure which differs widely in many respects from other more generally accepted theories. Starting with the assumptions that atoms, and also the protons ("archions") and electrons in atoms, possess axes and equatorial planes and with known facts regarding magnetic moments, ionizing potentials, valence, etc., he deduces electron distributions for the different kinds of elements. To enable electrons to have fixed equilibrium positions outside the nucleus, "innerkinetic" forces are assumed, these balancing the Coulomb forces at small distances. Although in the main the distributions of electrons in layers conform to previously proposed distributions, there are many differences in detail.

The nucleus is assumed to be composed of "helions"—units consisting of two protons and one electron—equal in number and identical in arrangement with the electrons outside. To account for isotopes and radioactivity, "neutrons," each consisting of one proton and one electron, are supposed to be in random motion in the space between the nucleus and the innermost layer of extra-nuclear electrons.

According to the author, atoms are usually held together in non-polar compounds by means of two coaxially placed valence electrons. Because of the peculiarities of the atomic structures assumed, many of the molecular structures proposed are quite different from all others which have previously been proposed for the same compounds, but the reviewer could not see that they fit the experimental facts better than the more common structures.

To one who is already familiar with the experimental facts and with other current theories on the subject, this book is interesting and suggestive in that it shows how many phenomena can be related or explained in quite unorthodox fashion. To others, however, this book can hardly be recommended, for throughout the work the author presents his theory without giving the reader much basis for comparison with other theories. The reviewer, for one, found many of the arguments which were given quite unconvincing.

MAURICE L. HUGGINS

Über Lösungs- und Verdünnungswärmen einiger starker Elektrolyte. (The Heats of Solution and Dilution of Some Strong Electrolytes.) By DR. ERICH LANGE, Lecturer at the University of Munich. Gebrüder Borntraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany, 1928. ii + 83 pp. 10 figs. 16.5 × 25.5 cm. Price, M. 6.40.

In this monograph the author outlines the thermo-chemistry of dilute solutions in a comprehensive manner. With copious references to a wide range of original articles, he reviews the theories of heats of solution and dilution of electrolytes and the experimental methods by which these theories can be tested.

The first section of the book is devoted to definitions, thermodynamic relationships and theoretical development. Here Dr. Lange shows how the heat of solution of an electrolyte has been calculated, by the methods of mathematical physics, from the lattice energy of the salt and the energy of solvation of the resulting ions. He briefly summarizes the "inter-ionic attraction" theory of Debye and Hückel and gives their equations for heats of dilution, pointing out the difficulties in extending these calculations above the extremely dilute "limiting range."

The second section, devoted to calorimetric methods, starts with a discussion of units of heat (the calorie and joule). Here the author unfortunately confuses with the joule the mayer (= 1 joule/degree) suggested by T. W. Richards to designate *heat* capacity in the c. g. s. system.

Dr. Lange rightly emphasizes the error in the usual method of calculating heats of solution of "insoluble" salts from the heats of precipitation without knowing the corresponding heats of dilution. These are by no means negligible. He shows that in the case of silver chloride this error amounts to a hundred calories and that it would be even greater with higher valent salts.

A good review of calorimetric principles and precautions and thermometry is followed by a brief description of his own adiabatic calorimeter (for measuring large heat changes) and his adiabatic differential calorimeter for very small heat changes. The latter is indeed remarkable as much for its fundamental simplicity and compactness (a two-liter vacuum flask divided in half by a sheet of hard rubber) as for the sensitivity of $^1/_2$ millionth of a degree attained by an iron-constantan thermel of 1000 junctions. To insure corresponding accuracy required meticulous attention to details—complete and rapid mixing, carefully controlled heat of stirring and a consideration of such possible disturbing factors as the adsorption of the solute ions on the walls of the calorimeter.

Curves of the integral and differential heats of dilution of most of the alkali halides are shown in three figures. The basic numerical values of the integral heats of dilution of these electrolytes are given in a table which includes also results for nine other salts of higher valence types. These results are found to agree essentially with those of Nernst, Orthmann and Naudé, in the few instances where comparison is at all possible.

Dr. Lange's results qualitatively check the predictions of the Debye-Hückel theory. Below 0.01 M the heats of dilution of all five uni-univalent salts investigated are positive, although the slopes of the actual curves are not exactly that of the theoretical "limiting law." There is, however, considerable uncertainty in the value of the dielectric constant of water and especially its temperature coefficient, from which the theoretical constant is derived. A conclusive test of the Debye-Hückel theory must await a more exact determination of this constant.

Dr. Lange's book will prove stimulating and useful to the thermochemist interested in the latest developments in extremely sensitive calorimetry. Whatever his specialty, the reader will find it a good summary of the increasingly large amount of theoretical work which has appeared, within the past few years, in the field of electrolytic solutions.

FRANK T. GUCKER, JR.

Soluble Silicates in Industry. By JAMES G. VAIL. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., New York, 1928. 443 pp. 185 figs. 16 X 23.5 cm. Price, $9.50.

In this book Mr. Vail has given a thorough, systematic and authoritative discussion of the history, constitution, properties, preparation and industrial utilization of the soluble silicates and their solutions. The thirteen hundred references attest a detailed study of the literature and a desire to give credit to other chemists for their investigations and ideas and yet the book is not a systematic and complete collation of the literature, good, bad and indifferent, of the Germanic type. The book gives the impression that it is written primarily out of the author's own experience and knowledge. Facts are stated with a clearness and positiveness derived from first-hand acquaintanceship; a corroborative reference is cited if available but it seems to make no real difference if corroboration of the author's views is not available. Here there is no hedging between the conflicting views of other authorities so characteristic of the mere compiler. Moreover, the facts are marshaled in accordance with *a* logical plan which greatly facilitates the use of the book.

The number and variety of uses of water glass which are discussed in detail will astonish most readers. In the discussion of uses, few receipts are given, but the function of each ingredient in the complex mixtures is clearly analyzed in a manner to aid the reader in adapting the composition to his own special requirements. This book is a valuable addition to the Monograph Series of the American Chemical Society.

GRINNELL JONES

Gesammelte Abhandlungen. (Collected Works.) Volume V. By Dr. F. KEHRMANN, Professor at the University of Lausanne. Georg Thieme, Leipzig, Germany, 1928. **321** pp. **53** figs. **17** X 25 cm. Price, unbound, M. 30.

The fifth volume of Kehrmann's collected papers contains reprints on a great variety of subjects. The first section presents, besides some early papers on complex acids which for one reason or another were not included in the first volume, Kehrmann's most recent work on the "basic properties of carbon" and on "oxonium compounds." The second section deals with recent investigations on quinonimide, fluorindine and carbazine dyes. The third, which is entitled "Miscellaneous," contains early and historically interesting papers on such topics as the structure of benzoquinone and the action of ammonium sulfide on halogen nitro compounds, as well as recent work on the blue oxidation product of diphenylamine.

On a concluding page Kehrmann presents the relation of his work to the three fundamental facts which in his opinion have contributed greatly to the present aspect of organic chemistry: the discovery of steric hindrance, oxonium salts and salts in which complexes of carbon and hydrogen can act as positive ions.

E. P. KOHLER

Elementary Organic Chemistry. By HOMER ADKINS, Ph.D., AND S. M. MCELVAIN, Ph.D., Department of Chemistry, University of Wisconsin. First edition. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1928. xi + 183 pp. 14.5 × 21 cm. Price, $2.25.

In this brief book of twenty chapters, the writers aim to present "organic chemistry in a one semester course," and "have laid emphasis upon the characteristic reactions of the important functional groups." The arrangement of the earlier chapters is essentially that so successfully used by the late Professor Ira Remsen. Sections of the text are designated by numbers and cross references are frequently indicated. The make-up of the book indicates a continuance of the high standard of the International Chemical Series. There are occasional misspellings and some slight errors in English, which it is hoped subsequent printings will rectify. The term "deracemize" has not the opposite meaning of racemize as the term is generally used, and has little to commend it. The type is good and the arrangement makes for particularly easy reading.

In the introductory part, at least by inference, the complete non-exist-
nce of inorganic isomers might be assumed. This is unfortunate. At
twice where hydrogen is indicated in an equation, it is written in
form, which is certainly not to be advocated when the product
the gas as it is in the cases cited. The reviewer is particularly
hat in dealing with the action of phosphorus trichloride on
planation is given for the observed evolution of hydrogen
ndard equation usually given for the preparation of
s not account for the production of this material.
s which elementary students in organic chemistry
insufficient acquaintance with inorganic chem-
ted that the fact that tertiary amines do not
ot specifically stated. Primary and secondary
student is apparently expected to infer that
e nitrogen the reaction does not proceed.
lcohols, the term "active" is used with no
rently the authors do not care to discuss
but the better student, the one who is really
rtainly call for an explanation from his instruc-
n were very briefly given in the text, it would be

helpful to all concerned. On at least two occasions, namely, in the preparation of iodoform and in the preparation of phenylhydrazine, the reduction is indicated simply by "2H." This is a particularly unhappy method of expression, since it tells very little, and the student interested in the subject will raise the question "How is this hydrogen obtained?" and the one not quite so concerned will assume that the reaction proceeds merely by supplying hydrogen gas. In most cases in this text the particular reagent for accomplishing a particular end is indicated. This is as it should be, and if sodium arsenite and stannous chloride were indicated in the cases just mentioned, these two instances would not stand out as they now do. The objection to the rigid Kekulé formula for benzene (*i. e.*, with fixed alternate double and single bonds), namely, that such a substance should be readily oxidizable, is not as pertinent as the fact that such a structure would lead theoretically to a greater number of disubstitution products than have been found in the case of benzene derivatives. It would seem advisable to suggest this at any rate. Under azo dyes a somewhat complicated formula is given and the preparation of this compound is described in detail. There seems to be no good reason why the fact that it is known as Congo Red and that this is an important direct dye for cotton should not be brought to the student's attention.

The criticisms indicated are the more noticeable because, as a whole, the book is accurate and shows careful preparation. The authors are to be commended on the restraint shown by them in keeping the text elementary and concise. This volume should be decidedly useful in the teaching of so-called "short courses" in organic chemistry.

G. ALBERT H

The Journal of the American Chemical Society

VOL. 51 MARCH, 1929 No. 3

THIRTY-FIFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1928

BY GREGORY PAUL BAXTER

RECEIVED FEBRUARY 12,1929 PUBLISHED MARCH 6, 1929

The German Committee on Atomic Weights has issued its Annual Report.[1] During the past year the following investigations were published.

Addingley and Whytlaw-Gray,[2] by a differential method, have found the ratio of the deviations from Boyle's Law for oxygen and hydrogen to be 1.00148 for the pressure range 0–1 atmosphere.

Potassium.—Hönigschmid and Goubeau[3] have confirmed by analysis of potassium bromide the value recently found by them by analysis of the chloride. Potassium oxalate was recrystallized five times with rejection of mother liquors and small head fractions in each case. Conversion to bromide with an excess of the purest bromine was followed by double crystallization of the bromide. The salt was dried in a current of pure nitrogen at gradually increasing temperatures and finally was fused in this atmosphere. Comparison with silver was followed by the determination of the silver bromide formed. Weights in air are corrected to vacuum.

TABLE I

THE ATOMIC WEIGHT OF POTASSIUM

Wt. of KBr	Wt. of Ag	Ratio KBr:Ag	At. wt. K	Wt. of AgBr	Ratio KBr:AgBr	At. wt. K
6.43476	5.83244	1.103271	39.103	10.15286	0.633788	39.107
7.37102	6.68104	1.103274	39.105	11.63067	.633757	39.101
4.70287	4.26274	1.103250	39.103	7.42057	.633767	39.102
5.72267	5.18704	1.103263	39.104	9.02972	.633759	39.102
5.05508	4.58197	1.103250	39.103			
4.96244	4.49799	1.103257	39.103	7.83013	.633762	39.102
5.60505	5.08032	1.103287	39.107	8.84400	.633769	39.103
4.68275	4.24433	1.103295	39.108	7.38862	.633779	39.105
6.37343	5.77696	1.103250	39.103	10.05611	.633787	39.107
6.60947	5.99069	1.103290	39.107	10.42840	.633795	39.108
	Average	1.103270	39.105		.633774	39.104

---

[1] *Ber.*, **61B**, 1 (1928).

[2] Addingley and Whytlaw-Gray, *Trans. Faraday Soc.*, *24*, 378 (1928).

[3] Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, *177*, 102 (1928).

Hevesy and Logstrup[4] through ideal distillation have effected a slight concentration of the heavier isotope of potassium. The atomic weight of the residual material has been determined by Honigschmid and Goubeau to be 39.109 instead of the normal value found by them, 39.105.

Titanium.—Baxter and Butler[5] by the analysis of titanium tetrabromide have confirmed the result obtained by them through the analysis of the tetrachloride (see report for 1927). The tetrabromide was prepared by the action of bromine carried by helium on (1) titanium, and (2) a mixture of titanium dioxide and carbon. The product was fractionally distilled eighteen times in an exhausted glass apparatus, without exposure to air after the ninth distillation. In each distillation a head and a tail fraction were removed in sealed glass bulbs. Certain head and tail fractions obtained after the tenth distillation were analyzed by comparison with silver. Weights are corrected to vacuum. The numbers of the fractions increase with decreasing volatility.

TABLE II

THE ATOMIC WEIGHT OF TITANIUM

Fraction	Wt. of $TiBr_4$	Wt. of Ag	Ratio $TiBr_4$:4Ag	At. wt. Ti
Head 11	10.02147	11.76512	0.851796	47.903
13	9.20373	10.80493	.851808	47.908
14	9.59208	11.26116	.851784	47.898
17	5.29301	6.21411	,851773	47.893
18	6.14520	7.21447	.851788	47.900
Tail 20	4.72253	5.54427	.851786	47.899
22	6.53582	7.67324	.851768	47.891
24	5.09864	5.98582	.851786	47.899
25	4.33488	5.08901	.851812	47.910
27	8.22722	9.65886	.851780	47.896
		Average	.851788	47.900

Copper.—Ruer[6] finds that copper which has been ignited in hydrogen at 750° to constant weight takes up not more than 0.001% of air (oxygen). The experimental values for the atomic weights of copper found by Ruer and Bode (see report for 1924) are lowered by only 0.002 if corrections for air adsorbed by copper oxide and copper are made.

Cesium.—Richards and Françon[7] extracted cesium salt from pollucite (Maine, U. S. A.) and purified cesium alum by several recrystallizations. Sulfate was removed by means of barium chloride and the cesium precipitated as perchlorate, which was recrystallized several times. Cesium chloride was obtained by thermal decomposition of the perchlorate and twice recrystallized. Drying by fusion in nitrogen containing a small

---

[4] Hevesy and Lögstrup, *Z. anorg. allgem. Chem.*, *171*, 1 (1928).

[5] Baxter and Butler, THIS JOURNAL, 50, 408 (1928).

[6] Ruer, *Z. anorg. allgem. Chem.*, *169*, 251 (1928).

[7] Richards and Françon, THIS JOURNAL, 50, 2162 (1928).

proportion of hydrochloric acid in a bottling apparatus was followed by weighing and comparison with silver in the usual way. Weights are corrected to vacuum.

TABLE III

THE ATOMIC WEIGHT OF CESIUM

Wt. of CsCl	Wt. of Ag.	Ratio CsCl: Ag	At. wt. Cs
4.42344	2.83610	1.55969	132.802
5.01421	3.21416	1.56004	132.840[a]
4.14983	2.66099	1.55951	132.783
4.48842	2.87747	1.55985	132.820
	Average	1.55977	132.811

[a] Corrected for error in calculation.

Barium and Silver.—Honigschmid and Sachtleben[8] dried barium perchlorate at 260° and converted it to chloride with hydrogen chloride at 550". Both substances were weighed in exhausted vessels to avoid air adsorption. The barium chloride was then compared with silver in the usual way and the silver chloride was weighed in a few experiments.

TABLE IV

THE ATOMIC WEIGHTS OF SILVER AND BARIUM

Wt. of $Ba(ClO_4)_2$	Wt. of $BaCl_2$	Wt. of O_4	Wt. of Ag	Ratio $Ag:O_4$	At. wt. Ag
7.14254	4.42378	2.71876	4.58277	1.68561	107.879
12.02482	7.44756	4.57726	7.71567	1.68565	107.882
10.32340	6.39382	3.92958	6.62360	1.68558	107.877
10.64966	6.59588	4.05378	6.83327	1.68563	107.882
11.69950	7.24609	4.45341	7.50692	1.68566	107.882
			Average	1.68564	107.880

	Ratio $Ba(ClO_4)_2:BaCl_2$	Ratio $Ba(ClO_4)_2:2Ag$	Ratio $BaCl_2:2Ag$	Wt. of AgCl	Ratio $Ba(ClO_4)_2:2AgCl$	Ratio $BaCl_2:2Ag$
	1.61458	1.55856	0.96531			
	1.61460	1.55849	.96525			
	1.61459	1.55858	.96531	8.80070	1.17302	0.72651
	1.61459	1.55850	.96526	9.07900	1.17300	.72650
	1.61459	1.55850	.96525	9.97378	1.17303	.72651
Average	1.61459	1.55853	.96528		1.17302	.72650
At. wt. Ba	137.355	137.354	137.355		137.360	137.357

The average result for barium, 137.36, is about 0.01 unit lower than that found by Richards thirty-five years ago.

Cerium.—Honigschmid and Holch,[9] using cerium material which had been freed from lanthanum and neodymium by fractional crystallization of the double magnesium nitrates, have analyzed cerous chloride. The

---

[8] Honigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **178,** 1 (1929).

[9] Honigschmid and Holch, *ibid.*, **177,** 91 (1928).

recrystallized chloride was dehydrated at gradually increasing temperatures, first in a current of nitrogen and hydrogen chloride, then in pure hydrogen chloride, and ultimately was fused. Comparison with silver was followed by the determination of the silver chloride. Weights in air are corrected to vacuum.

TABLE V

THE ATOMIC WEIGHT OF CERIUM

Wt. of $CeCl_3$	Wt. of Ag	Ratio $CeCl_3:3Ag$	At. wt. Ce	Wt. of AgCl	Ratio $CeCl_3:3AgCl$	At. wt. Ce
3.43507	4.51018	0.76163	140.122	5.99272	0.57321	140.114
2.39181	3.14058	.76158	140.107	4.17266	.57321	140.116
3.05998	4.01767	.76163	140.123	5.33803	.57324	140.130
4.17583	5.48247	.76167	140.136	7.28454	.57325	140.131
1.34828	1.77015	.76168	140.138	2.35210	.57322	140.122
2.04994	2.69147	.76164	140.127	3.57628	.57320	140.113
2.38287	3.12846	.76168	140.138	4.15673	.57326	140.135
2.57235	3.37733	.76165	140.130	4.48755	.57322	140.120
2.16635	2.84432	.76164	140.127	3.77918	.57323	140.126
		.76164	140.127		.57323	140.123

This result is lower than that obtained by Brauner, 140.25, which has been in use for some time.

Erbium.—Boss and Hopkins[10] further fractionated material already limited in content to erbium and yttrium by (a) nitrate decomposition and (b) nitrite precipitation. Head fractions were converted to chloride and portions which had been dehydrated by gradual heating to the fusion point were weighed and compared with silver. Weights in air are corrected to vacuum.

TABLE VI

THE ATOMIC WEIGHT OF ERBIUM

Method of purif.	Wt. of $ErCl_3$	Wt. of Ag		Ratio $ErCl_3:3Ag$	At. wt. Er
a	2.25485	2.66270		0.84683	167.69
a	0.30165	0.35630		.84663	167.63
a	1.02242	1.20761		.84665	167.64
b	0.38998	0.46068		.84654	167.60
b	.38219	.45144		.84662	167.63
b	.17445	.20604		.84668	167.65
			Av.	.84666	167.64

The result is very slightly lower than the current one.

Rhenium.—W. and I. Noddack[11] have determined the atomic weight of rhenium by several methods, of which they consider the reduction of the disulfide the most reliable.

---

[10] Boss and Hopkins, THIS JOURNAL, 50, 298 (1928).

[11] Noddack and Noddack, Z. *Elektrochem.*, 34, 627, 630 (1928).

TABLE VII

THE ATOMIC WEIGHT OF RHENIUM

	Ratio Re:S_2	At. wt. Re
	2.9432	188.7
	2.9405	188.6
	2.9458	188.9
	2.9395	188.5
Av.	2.9423	188.7

Lead.—Lotze[12] on the basis of determinations of the uranium and thorium content and of the atomic weight of the lead contained in uranium minerals computes the atomic weight of actinium lead to be 207.

Uranium.—Honigschmid and Schilz[13] have continued the work of Honigschmid (see report for 1914) on uranium by the preparation and analysis of uranous chloride. Two preparations were employed: A, used in the earlier investigation, was obtained from commercial nitrate; B was obtained from Norwegian euxemite and samarskite. Both specimens were subjected to the same elaborate purification and ultimately converted to oxide. To prepare the uranous chloride the oxide was mixed with pure sugar charcoal and heated in a current of chlorine in a quartz sublimation apparatus. The first product was then sublimed into a quartz weighing tube and fused in an atmosphere containing varying proportions of nitrogen and chlorine as follows.

In Series I the chloride was resublimed and fused in pure nitrogen. In Series II resublimation in pure chlorine was followed by fusion in pure nitrogen or very dilute chlorine and the salt was solidified in pure nitrogen. In Series III, after resublimation in a mixture of nitrogen and chlorine, the chloride was twice melted and cooled in pure nitrogen.

To analyze the product, the solution, after acidification with nitric acid and oxidation with hydrogen peroxide, was compared with silver

TABLE VIII

THE ATOMIC WEIGHT OF URANIUM

Series I

Preparation	Wt. of UCl_4	Wt. of Ag	Ratio UCl_4:4Ag	At. wt. U	Wt of AgCl	Ratio UCl_4:4AgCl	At. wt. U
A	1.86485	2.11805	0.880456	238.11	2.81388	0.662733	238.14
A	2.49763	2.83641	.880560	238.15	3.76866	.662737	238.16
A	4.75974	5.40512	.880598	238.17	7.18174	.662756	238.16
A	4.97877	5.65443	.880508	238.13	7.51270	.662714	238.14
A	4.90253	5.56780	.880515	238.13	7.39765	.662715	238.14
B	3.09615	3.51621	.880536	238.14	4.67190	.662718	238.14
B	2.61129	2.96561	.880524	238.14			
B	3.28471	3.73029	.880551	238.15	4.95638	.662724	238.14
		Av.	.880535	238.14		.662728	238.15

---

[12] Lotze, Z. *anorg. allgem. Chem.*, 170, 213 (1928).

[13] Honigschmid and Schilz, *ibid.*, 170, 145 (1928).

TABLE VIII (Concluded)

Preparation	Wt. of UCl_4	Wt. of Ag	Ratio $UCl_4:4Ag$	At. wt. U	Wt. of AgCl	Ratio $UCl_4:4AgCl$	At. wt. U
			Series II				
A	3.36146	3.81768	0.880498	238.12	5.07211	0.662734	238.15
A	3.48180	3.95413	.880548	238.15	5.25351	.662757	238.16
A	3.05228	3.46649	.880510	238.13	4.60579	.662705	238.13
A	2.23307	2.53616	.880493	238.12	3.36983	.662666	238.11
A	2.87576	3.26616	.880471	238.11	4.33961	.662677	238.12
B	5.17799	5.88081	.880489	238.12	7.81333	.662712	238.14
B	6.06599	6.88877	.880562	238.15	9.15306	.662728	238.15
B	5.35148	6.07749	.880541	238.14	8.07478	.662740	238.15
		Av.	.880514	238.13		.662720	238.14
			Series III				
B	4.59686	5.22090	0.880473	238.11	6.93657	0.662699	238.13
B	3.94272	4.47757	.880549	238.15	5.94951	.662697	238.13
B	3.68049	4.17994	.880513	238.13	5.55357	.662725	238.14
		Av.	.880507	238.13		.662707	238.13

and the silver chloride was collected and weighed. Weights in air are corrected to vacuum.

The final average, 238.14, is slightly lower than the earlier one.

Ruer and Kuschman[14] have investigated the adsorption of air on inorganic solids. One of the important findings is that fused powdered potassium chloride and precipitated dried lead chloride adsorb less than 0.5 mg. of air per 100 g. of solid.

Hogness and Kvalnes[15] confirm Aston's suspicion of the existence of an isotope of neon of mass 21 and estimate the proportions of the three isotopes as Ne^{20}, 88%, Ne^{21}, 2%, Ne^{22}, 10%.

Aston[16] has discovered additional isotopes of zinc and germanium which are listed below in the order of abundance, together with those already known.

Zn	64,	66,	68,	67,	65,	70,	69	
Ge	74,	72,	70,	73,	75,	76,	71,	77

In the table of atomic weights on p. **653** changes from the 1928 table are made in the cases of hydrogen, phosphorus, sulfur, barium, cerium, erbium, potassium, radium, thorium and uranium. The value for hydrogen depends largely upon the evidence of the mass spectrograph. In the cases of phosphorus and sulfur, the uncertainty of existing data makes the third decimal place of dubious value. The value for potassium is given to two decimal places only, since the cause of the discrepancy between that found by Richards, Staehler and Mueller, 39.095, and the recent one by Hönigschmid and Goubeau, 39.105, is not evident. The atomic weight of

---

[14] Ruer and Kuschman, *Z. anorg allgem. Chem.*. **166**, 257 (1927).

[15] Hogness and Kvalnes, *Nature*, **122**, 441 (1928).

[16] Aston, *Ibid.*, **122**, 167, 345 (1928).

American Chemical Society
Atomic Weights
1929

	Symbol	At number	At. weight		Symbol	At. number	At. weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.77	Neodymium	Nd	60	144.27
Argon	A	18	39.94	Neon	Ne	10	20.183
Arsenic	As	33	74.96	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.07	Potassium	K	19	39.10
Carbon	C	6	12.000	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	188.7
Chromium	Cr	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.1	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.26	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.5
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	82.9	Uranium	U	92	238.14
Lanthanum	La	57	138.90	Vanadium	V	23	50.96
Lead	Pb	82	207.22	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.6
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

radium includes the correction determined by Honigschmid for the temperature of the radium salt. This was overlooked in the earlier tables. The value for thorium is that obtained by Honigschmid in his most reliable series.[17]

T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

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

ACTIVE NITROGEN. II. THE INFLUENCE OF SURFACE ON THE AFTERGLOWS IN NITROGEN AND OXYGEN[1,2]

BY BERNARD LEWIS[3]

RECEIVED JULY 21, 1928 PUBLISHED MARCH 6, 1929

It has been contended by some workers[4] that pure nitrogen subjected to the action of an electric discharge shows no afterglow but that its restoration is effected by the addition of a trace of oxygen. Other investigators[6] have shown that pure nitrogen undoubtedly could give rise to an afterglow, which, however, is intensified by the addition of oxygen or certain other impurities. More recently Bonhoeffer and Kaminsky[6] have concluded that pure nitrogen is glowless but the introduction of certain optimum amounts of such impurities as oxygen, hydrogen sulfide and methane into the discharge mixture produces a glow of maximum intensity.

The action of the impurities has been thought to be due to the formation of a layer of gas on the surface of the vessel which inhibits the catalytic combination of nitrogen atoms thereon. The atoms must now combine in the gas phase with consequent emission of the a-bands. It was the purpose early in these experiments to ascertain whether the impurity, oxygen, entered into the mechanism of afterglow production. The possibility could not be entirely excluded that oxygen was necessary in some physical action to induce the afterglow in the gas phase, notwithstanding results by Bonhoeffer and Kaminsky, namely, that different impurities are without effect on the character of the afterglow.

---

[17] Hönigschmid *Sitz. Kaiser. Aked. Wien,* [IIa] 125, 1 (1916).

[1] Read before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 8, 1928.

[2] Bernard Lewis, Part I, THIS JOURNAL, 50, 27 (1928).

[3] National Research Fellow in Chemistry.

[4] Compte, *Physik.* Z., 14, *74* (1913); Tiede, *Ber.,* 46, 340 (1913); Tiede and Domcke, *ibid.,* 46, 4095 (1913); 47, 420 (1914).

[5] Von Mosengeil, *Ann. Physik,* 20, 833 (1906); Strutt, *Proc. Roy. Soc.,* 85, 219 (1912); *Physik.* Z., 14, 215 (1913); Konig and Elod, ibid., 14, 165 (1913); *Ber.,* 47, 523 (1913); Konig, *Z. Elektrochem.,* 21, 278 (1915); Baker and Strutt, *Ber.,* 47, 801, 1049 (1914); Baker, Tiede, Strutt and Domcke, *Nature,* **93,** 478 (1914); Strutt, *Proc. Roy. Soc., 91,* 303 (1915).

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

Initial Experiments.[7]—Accordingly, pure nitrogen was introduced into a liter bulb[8] into the center of which pure oxygen could be admitted more or less uniformly in all directions through an inner tube perforated at one end. In impure nitrogen the active species which eventually give rise to the glow remain for some time after the cessation of the discharge. If similar circumstances exist in pure nitrogen (assuming it is glowless) and provided the presence merely of ordinary oxygen is required to create the afterglow, then the glow may be expected to appear if oxygen is introduced immediately after discontinuing the discharge.

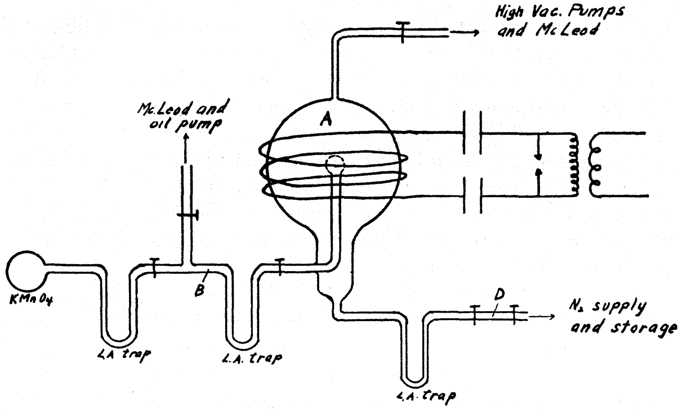


Fig. 1.

The apparatus given in Fig. 1 requires no explanation. Pure oxygen was prepared from potassium permanganate and pure nitrogen by two methods: (1) from bromine water and ammonia,[9] and (2) by heating sodium trinitride (NaN_3). Water vapor was removed from the gases in liquid-air traps. In the first method the nitrogen, prepared in a special generator, was also stored over phosphorus pentoxide to remove ammonia. The electrodeless discharge was employed in all experiments, thus eliminating a possible contaminating influence of metallic electrodes. A static method was used.

For some time it was impossible to produce absolutely glowless nitrogen, even though utmost precaution had been taken to ensure the complete absence of oxygen and other impurities. Only after thoroughly baking out the bulb at high temperature and under high vacuum as well as the occasional passage of the discharge was a glowless pure nitrogen obtained[10] (nitrogen pressure about 0.1 mm. of mercury). Upon the

---

[7] Bernard Lewis, *Nature*, 121, **938 (1928).**

[8] The bulb and all connecting tubes, made of pyrex, were carefully cleaned with hot chromic acid and subsequently heated almost to melting before assembling the apparatus.

[9] Waran, *Phil. Mag.*, 42, 246 **(1921);** Kenty and Turner, *Nature,* **120, 332** (1927).

[10] With this treatment the glow gradually disappeared. It must be remarked that in using a static system in a glass vessel, it is not easy to remove the glow entirely by heating alone. It was noted on several occasions that whereas no glow was evident after the discharge was discontinued, during the passage of the latter the characteristic nitrogen glow could be observed, though weak, to extend about 1.5 cm. into the wide tubing directly below the bulb.

introduction of pure, dry oxygen (1%, the pressure was adjusted in dosing tube B) in the manner described above, ***no glow was produced.*** This was repeated several times using nitrogen from both sources with similar results. Furthermore, after the oxygen had been admitted and the mixture subjected to the discharge, little or no glow was discernible.[11] This seemed very strange indeed in view of the previous work of Strutt, Bonhoeffer and Kaminsky and others. It is evident that neither ordinary oxygen molecules nor "active" oxygen takes part in the excitation process which produces the luminosity. This conclusion is not at variance with Bonhoeffer and Kaminsky's observation mentioned above regarding the effect of impurities on the afterglow spectrum.

Further Experiments.—The electrical arrangement was modified somewhat in order to increase the energy in the coil wrapped around the bulb, so that the discharge could be passed at higher gas pressures. A spark gap made with heavy zinc electrodes 4 cm. in diameter was connected in series with two condensers (each of 10 double-thickness glass plates 18 X 20 inches, immersed in transformer oil) which in turn were in series with the coil. The latter (4 turns) and leads (which were made as short as possible) consisted of 0.25-inch copper rod. The secondary of a transformer was connected across the spark gap, which was 2.5 to 3 cm. wide. The secondary voltage was about 50,000 volts and the primary current 21.5 amperes. A glass tube 20 cm. long and about 7 cm. in diameter was substituted for the bulb. Two liquid-air traps protected the tube from stopcock grease. Nitrogen could be obtained at will from sodium nitride or from a nitrogen cylinder (containing 0.3% of oxygen by analysis) and the oxygen was obtained from potassium pennanganate. All gases entered the discharge tube by way of the dosing Tube B in which water vapor, etc., was removed with liquid air. In all of the experiments to be described the discharge tube was initially baked out at a temperature of 350–470° from six to eighteen hours under high vacuum. All connecting tubes were heated frequently almost to melting. Unless otherwise stated, (1) the gas admitted was previously deprived of water vapor by long standing (six to twenty-four hours) at liquid-air temperature and (2) both traps in direct communication with the discharge tube were immersed in liquid air.

During the progress of the following work a paper appeared by G. Herzberg[12] on the influence of the walls on the nitrogen and oxygen afterglows. The results recorded here, in so far as the two works overlap, substantiate Herzberg's observations. The method employed to restore the afterglow was unlike that used by him. Some interesting new phenomena in temperature and pressure effects have also been found.

A.—Tank nitrogen was admitted at a pressure of 0.704 mm. The glow was weak and lasted for fourteen seconds.[13] Normally in an unbaked vessel and with water removed from the entering gas, the afterglow lasted for about 130 sec. and with greater intensity. With intermittent discharging the duration and intensity of the glow gradually diminished to < 0.5 sec. The vessel now being evacuated to 0.31 mm., no glow was visible. Upon removing the liquid air from both traps the glow reappeared,

---

[11] It will be shown in a subsequent contribution (Part III) that a mixture containing 1% of oxygen at a pressure of about 0.1 mm. gives rise to an intense afterglow of long duration under ordinary circumstances.

[12] G. Herzberg, *Z. Physik,* 46, 478 (1928).

[13] Observation of the enhanced afterglow at the liquid-air trap with a spectroscope indicated the presence of a-bands.

lasting for eighteen sec. (Under ordinary conditions and at this pressure the glow would last for 190 sec.) By the same procedure (discharging[14] with liquid air on the traps) the glow could again be eliminated, a pressure decrease < 0.01 mm. being recorded on the McLeod gage. Thus it is evident that some gas is being condensed out.

B.—Tank nitrogen was admitted at a pressure of 0.318 mm. The glow lasted for twelve sec. Fresh tank nitrogen was admitted at a pressure of 0.349 mm., the glow lasting for ten seconds. This was increased to twenty sec. when the liquid air was removed from both traps. This is to be expected, since in a system containing a given amount of active gas, the glow is enhanced at liquid-air temperature resulting in a more rapid removal of the glow-producing species. Ordinary tank nitrogen (moist) was now admitted, with the following results:

Pressure (mm.)	0.357	0.290	0.129
Duration (sec.)	90	130	160

The vessel was evacuated and fresh moist tank nitrogen admitted:

Pressure (mm.)	1.3	0.328	0.205
Duration (sec.)	72	115	140–150

Liquid air was replaced on both traps and this gas (0.205 mm.) was subjected to the discharge, the glow becoming weaker and of shorter duration until finally it disappeared entirely. The pressure had decreased to 0.16 mm.[15] In this glowless condition fresh, dry tank nitrogen was admitted at about 3 mm. and the vessel evacuated to a pressure 0.22 mm. *Practically no afterglow was observed.* If any was present it was exceedingly faint and lasted less than a fourth of a second (possibly due to weak phosphorescence of the glass, which is sometimes observed). Repetition of the above on other occasions failed to show any glow whatsoever. When the liquid air was removed the glow reappeared with its usual intensity and endured for 117 sec. These experiments indicate conclusively that even in the presence of sufficient oxygen to produce a very marked glow under ordinary conditions, the afterglow can be eliminated if the vessel is treated as outlined above.

[14] Herzberg also found that in order to eliminate the afterglow in a glass vessel, completely, the discharge had to be passed, for only in this way can the last traces of water vapor or other occluded gas be removed from the walls.

[15] It is not understood why such a decrease in pressure should have occurred unless it be due to the usual "clean-up" effect. In the initial experiments recorded above, this pressure decrease was so marked at times, after long discharging, that the discharge ceased to pass. Thus it was observed that the pressure sometimes decreased from 0.1 to 0.001 mm. The gas could be recovered by removing the liquid air and heating the bulb. Some investigation of this was carried out but the results are not sufficient to warrant mention here. Herzberg also noted this extraordinary "self-evacuation."

C. I.—Experiment B was repeated but the traps were cooled to a temperature of only —85° (carbon dioxide and ether). Dry tank nitrogen showed a weak glow lasting for nine sec. which disappeared as before after some discharging. The condensate therefore cannot be ozone, nitric oxide or nitrous oxide. Other possibilities are water, nitrogen peroxide, nitric acid, and nitrogen pentoxide. We are interested here in the substance which, when removed, causes the glow to disappear. Since (1) the glow can be eliminated even in the presence of oxygen, (2) the same effect takes place in pure nitrogen (see Section D) and (3) the glow, it will be shown, can be restored by addition of small amounts of water vapor to pure or tank nitrogen, it is probable that the effective substance is water vapor. The Last traces of water which adhere tenaciously to the glass walls are liberated by the discharge and condensed. It is quite possible that nitrogen peroxide also is condensed out from tank nitrogen as Majewska and Bernhardt believe.[16]

C. **II.** Reversed Pressure Effect with **Tank** Nitrogen.—Fresh dry tank nitrogen was admitted to the vessel in the condition as left in C I.

Pressure (mm.)	0.390	0.267
Duration (sec.)	1	0.6

The carbon dioxide–ether baths were removed and replaced by liquid air after the trap had warmed up. The glow which appeared (seven sec.) was removed completely by discharging. Fresh, dry tank nitrogen was admitted again.

Pressure (mm.)	>1.0	0.40	0.275
Duration (sec.)	7	1.4	<0.25

The vessel was evacuated and fresh, dry tank nitrogen admitted again. At a pressure of 0.148 mm. there was no glow. This procedure was repeated; at a pressure of 0.445 mm. the glow lasted for one sec., while at 0.210 mm. there was no glow.

These results are in agreement with those in Section B as long as the pressure of nitrogen is low (about 0.20 mm). However, when the pressure is increased, an afterglow undoubtedly appears even though of short duration. This may be explained as follows. At higher pressures some of the clean surface is poisoned by adsorption of the gases (both oxygen and nitrogen). The combination of nitrogen atoms on the walls being somewhat hindered, more combinations can occur in the gas phase and give rise to the afterglow. At lower pressures the decreased adsorption exposes more free surface for atomic combination. The same effect is observed when pure nitrogen is used (see Section D).

The interesting fact established is, that *with a "clean" surface a pressure effect is observed which is reversed from that observed with an "unclean"*

---

[16] Majewska and Bernhardt, Z. *Physik,* 48, 140 (1928).

surface. That is to say, with the latter the afterglow increases in duration and intensity with reduction in pressure (see Section B and also Part III), whereas with the former the duration and intensity decrease with pressure.

D. Reversed Pressure Effect with Pure Nitrogen—Pure dry nitrogen (from sodium nitride) was admitted.

Pressure (mm.)	1.7	0.260	0.158
Duration (sec.)	12	5	3.5

Thus the reversed pressure effect is also evident with pure nitrogen. In this case also the glow disappeared completely by passing the discharge. As mentioned in Section C this is probably due to the removal of the last traces of adsorbed water. However, even under these circumstances, the admittance of a fresh supply of pure nitrogen at higher pressures causes a short glow to appear.

Pressure (mm.)	1.43	0.152
Duration (sec.)	4	<0.25

E. Restoration of the Afterglow by Water Vapor.—These experiments were designed to ascertain whether the introduction of water vapor sufficient to cover the surface could restore the afterglow in pure nitrogen. A small glass tube containing distilled water whose dissolved oxygen was removed by boiling, was connected through a stopcock to the discharge vessel. The water could be maintained at any desired temperature and the vapor pressure above ice calculated from the equation of Nernst[17]

$$\log_{,,} p_{\mathrm{mm.}} = -\frac{2611}{T} + 1.75 \log T - 0.00210\, T + 6.5343$$

which has been substantiated experimentally down to 100°K. by Weber.[18] Nitrogen at a pressure of 0.26 mm. gave only a faint glow lasting for three sec. in the thoroughly baked vessel (liquid air removed from traps). The vessel and water tube were now thoroughly evacuated, the latter being maintained at liquid–air temperature. The liquid air was replaced by a carbon dioxide–alcohol mixture at −39° and water vapor at a pressure 0.11 mm. was admitted to the discharge vessel. The excess water vapor in the gas phase was condensed out in a liquid-air trap and then pure dry nitrogen admitted. A bright afterglow lasting for 75–80 sec. was observed at 0.190 mm. pressure.[19] The whole procedure was repeated, this time admitting water vapor at a pressure $1.2 \mathrm{X} 10^{-3}$ mm. (ice at −73") with the following results:

Pressure (mm.)	1.2	0.54	0.158
Duration (sec.)	37	70	93–100

---

[17] Nernst, *Verh. deut. Phys. Ges., 11,* 313 (1907).

[18] Weber, *Comm. Phys. Lab. Univ. Leyden, 14,* 150A (1915).

[19] Herzberg was able to restore the glow by the addition of small amounts of hydrogen.

It should be noted in the last table that the normal pressure effect is again in evidence with a covered surface.

By discharging with liquid air on one trap the glow was reduced from one hundred sec. to nineteen sec. This was not carried on long enough to diminish the glow further. There was no measurable pressure decrease. Removal of the liquid air caused the restoration of the glow to 140 sec. Thus the afterglow is present or not depending upon the presence of water vapor on the walls. It was found that too much water vapor in the gas phase was prejudicial to the afterglow, a fact also observed by E. P. Lewis.[20]

F.—These experiments will show that the effects in Section E are reproducible with tank nitrogen and that the presence of **0.3%** of oxygen has no effect in prolonging the glow over that observed in pure nitrogen. After the same treatment as in Section E, water vapor at 2.2×10^{-3} mm. (ice at $-69°$) was admitted.

1. Dry pure nitrogen	Pressure (mm.)	1.23	0.27
	Duration (sec.)	36	90

Vessel evacuated.

2. Dry tank nitrogen	Pressure (mm.)	0.88	0.24
	Duration (sec.)	63	100

The increase of ninety to one hundred sec. is to be anticipated on reducing the pressure from 0.27 to 0.24 mm. Note the normal pressure effect in both cases.

G. Reversed Temperature Effect.—It is well known that when an untreated vessel containing nitrogen which gives rise to a long afterglow at room temperatures is heated, the afterglow is considerably reduced both in intensity and duration. For example, in one experiment it was found that the afterglow was diminished from 160 to two sec. at a pressure of nitrogen of 0.155 mm. when the vessel was heated from room temperature to approximately 250° (Bunsen burner used). However, in the course of this work it was found that in vessels which were treated as outlined in this paper, a different phenomenon prevails, namely, that not only is the afterglow not diminished by heating but the duration is increased and the intensity slightly enhanced. Many and varied experiments were carried out both with pure and tank nitrogen; but one example will be given. Pure nitrogen at 0.152 mm. pressure in a baked-out vessel gave rise to a glow lasting for one-half sec. When the vessel was heated with a free flame, it lasted for two and one-half sec. Tank nitrogen at 0.20 mm. pressure showed a glow which lasted for three sec. at room temperature and five and one-fifth sec. when heated. After the vessel had cooled, the glow lasted for two and four-fifth sec. and on heating again for three

[20] E. P. Lewis, *Ann. Physik*, 2, 459 (1900).

and four-fifth sec. The effect is very noticeable if the glow be eliminated completely by discharging with the liquid-air traps in operation. Were the glow can be restored to last almost one second on heating the vessel.

This reverse temperature effect can easily be explained by assuming that when the discharge is passed in a vessel whose walls are "clean," a layer of nitrogen atoms is adsorbed on the surface. Other atoms colliding with the wall will nearly always meet an adsorbed atom and combine to form a molecule. However, when heat is applied much more of the surface is free and atoms will not always "find" an adsorbed atom on colliding with the wall. This leads to many more favorable collisions in the gas phase and thus we observe an enhanced afterglow.

Finally, two sets of data will be given to show simultaneously both the reversed and normal effects of pressure and temperature.

1. Tank nitrogen. Baked vessel.

Pressure (mm.)	**1.5**	**0.20**
Duration (sec.)	**17**	**3**
After heating, duration (sec.)		**5.2**

2. Tank nitrogen after admittance of 2×10^{-3} mm. of water vapor.

Pressure (mm.)	**1.35**	**0.29**	**0.155**
Duration (sec.)	**4**	**100**	**160**
After heating, duration (sec.)			**2 3**

H. The Effect of a Paraffied Surface.—A bulb of 250-cc. capacity and about the same diameter as the discharge tube (a new tube was used which had never been baked out) was coated on the inside with paraffin and sealed to the latter tube. The afterglow was observed through a small opening made by warming the paraffin locally. It was found that with a pressure of tank nitrogen of 0.29 mm. the afterglow in the discharge vessel and the paraffined bulb was of the same intensity and duration (275 sec.). Apparently, therefore, not only does the paraffin effectively poison the surface but it does not itself act as a catalyzer for atomic combination.

Experiments with Oxygen

It was shown above that the nitrogen afterglow is made observable only after the surface of the vessel has been effectively poisoned by the adsorption of a layer of gas.

The results of the following experiments show that the afterglow in oxygen likewise is dependent on the surface condition. This may be expected if the view expressed by Thompson[21] is correct that the after-

---

[21] J. J. Thompson, *Phil.* **Mag., 32, 321 (1891); E. P. Lewis, Ann.** *Physik,* 2, **549 (1900);** **R.** J. **Strutt (Lord Rayleigh),** *Proc. Phys. Soc.,* 23, 66 **(1910). It is not certain that the afterglow observed in pure oxygen is the same as the continuous spectrum in air observed by Lord Rayleigh, which he attributed to the oxidation of NO by O_3 (formed in the discharge) to NO_2.** *G.* **Herzberg,** *Z. Physik,* **46,878 (1928);** J. **Kaplan,** *Proc. Nat.* **Acad.** *Sci.,* 14, **258 (1928);** B. **Lewis,** *Nature,* 121, **938 (1928).**

glow observed in pure oxygen is due to the emission accompanying atomic recombination, which is strengthened by the fact that the observed spectrum is continuous.[21] The presence of atoms has been demonstrated by Crew and Hulbert[22] and Copeland.[23] The duration of the afterglow in oxygen is considerably shorter than in nitrogen. This may be attributed to the possibly greater facility with which oxygen atoms combine.[24]

The experimental procedure was the same as outlined above. Pressures were read on a McLeod gage connected to the dosing tube. Observations were made in a completely darkened room, a small spectroscope being used to observe the character of the afterglow. Pure oxygen was prepared from potassium permanganate.

Results

In a discharge tube which had been thoroughly cleaned (hot chromic acid followed by distilled water and heating the glass almost to melting), pure oxygen showed an afterglow whose spectrum was continuous in character and whose duration changed with the pressure as follows:

Pressure (mm.)	0.925	0.475	0.285	0.19	0.15	0.115[25]
Duration (sec.)	8	17.2	25.2	32	36	30.4

Upon discontinuing the discharge, the intensity of the afterglow decreased gradually but after a time it suddenly came to an abrupt end. This is quite unlike the prolonged gradual decay of the nitrogen afterglow. Herzberg[12] recorded a similar observation.

The discharge tube was baked out in a furnace at a temperature of 400–440" for eight hours under high vacuum. Both traps were then immersed in liquid air and pure, thoroughly dried oxygen was admitted. At various pressures between 1 mm. and 0.216 mm. not the slightest indication of an afterglow was visible. A glow was still absent after the removal of the liquid air. This was the first experiment with oxygen. In later work this extreme success merely by baking the vessel was never completely realized.

In another representative experiment in a baked-out vessel a faint afterglow was observed lasting about half a second at a pressure of oxygen of about 1.8 mm. (The first two short discharges showed no glow.) At a pressure of 0.24 mm. the duration was two and one-half seconds. When the liquid-air traps were removed the duration was three and one-half seconds.[26]

---

[22] Crew and Hulbert, Phys. Rev., **30,** 124 (1927).

[23] Copeland, *ibid.,* **31,** 1113A (1928); Bichowsky and Copeland, *Nature,* 120, 729 (1927).

[24] Bernard Lewis, THIS JOURNAL, **51,** 665 (1929).

[25] This pressure is below the duration maximum of the oxygen afterglow at about 0.16 mm. (ref. 24).

[26] This may have been due in part to the adsorption of ozone condensed by liquid air.

With the liquid air replaced, only a little discharging was required to cause the glow to disappear entirely. Ordinarily in an untreated vessel the oxygen afterglow is destroyed by heat but when heat is applied to a treated vessel containing glowless oxygen, the glow appears. In the present instance it lasted about a quarter of a second. After cooling, it disappeared only to reappear again on heating. This ***reversed temperature effect*** in a vessel with "clean" walls was also observed in the nitrogen afterglow. The explanation advanced for the latter also applies here.

A fresh supply of pure dry oxygen was admitted to the discharge tube which previously contained oxygen whose glow had been removed by discharging. At a pressure of 0.66 mm. there was practically no glow (less than a tenth of a second) and at 0.26 mm. no glow at all. It is quite evident that an afterglow cannot be obtained with pure oxygen in a vessel whose walls are "clean." A "reversed pressure effect" cannot definitely be said to exist due to the exceedingly faint and short afterglow.

An attempt was made to see whether the glow could be restored by the introduction of water vapor sufficient to cover the surface. The general procedure was the same as given above. It was shown first that pure dry oxygen produced only a very faint glow in the baked-out vessel. Water vapor at a pressure 8×10^{-3} mm. (ice at −60°) followed by pure oxygen was then admitted. A bright afterglow was produced[19] whose duration is given in the following table.

Pressure (mm.)	0.66	0.314	0.226	0.111[25]
Duration (sec.)	3	11.4	15	13

Too much water in the gas phase is prejudicial to the afterglow. Thus at a pressure of oxygen of 0.25 mm. and of water vapor of 0.135 mm. (ice at −37°) the glow lasted less than one second; after condensing most of the water vapor in liquid air the duration was 7 seconds.

The results with air in *a* baked-out vessel indicated also that the afterglow is considerably weakened in intensity and duration. It will be shown elsewhere[21,24,27] that the afterglow in air undergoes several changes as the pressure is decreased. In a vessel which was baked out but which was not subjected to the discharge treatment, these changes were still observed but the glows were exceedingly weak. At the minimum separating the oxygen afterglow from the nitrogen afterglow, the glow disappeared entirely.

Finally the effect of a paraffin surface was studied. It was found that the afterglow behaved similarly in the paraffined vessel as in the discharge vessel. The durations and intensities were identical and the same abrupt termination of the afterglow was observed in each.

---

[27] Constantinides, *Phys. Rev.*, 30, 95 (1927), and Bernard Lewis, *Nature*, 121, 938 (1928).

When liquid air was placed on one of the traps the afterglow intensity was not enhanced near the surface of the liquid air, as is the case with the nitrogen afterglow. Instead, it seemed as if it was reduced in intensity or even extinguished. One could not be certain about this last point since the tube was always slightly frosted over. However, it may be noted that Herzberg (ref. 21 p. 892) reports that when the discharge tube is cooled with liquid air no glow is observed.

Summary and Conclusions

The experiments described above show that:

1. Ordinary oxygen or "active" oxygen takes no part in the excitation process which gives rise to the nitrogen afterglow.

2. Pure nitrogen prepared from sodium nitride and nitrogen containing *0.3%* of oxygen show intense afterglows of long duration in an ordinary glass vessel. Pure oxygen shows a characteristic green afterglow (continuous spectrum) in a similar vessel.

3. Pure nitrogen or nitrogen containing *0.3%* of oxygen at about *0.2* mm. pressure can be made to show no glow if the vessel is thoroughly baked out and subjected to the action of the electric discharge. Above this pressure a short glow appears. The afterglow in oxygen disappears in a similarly treated vessel.

4. Admittance of water vapor (*ca.* 10^{-3} mm.) enough to cover the surface of the vessel causes a restoration of the glow to its usual intensity and duration both in pure nitrogen and nitrogen containing 0.3% of oxygen. The afterglow in oxygen may similarly be restored by water vapor. Too much water vapor is prejudicial to the nitrogen and oxygen afterglows.

5. *The condition of the surface of the containing vessel is a determining factor which governs the visibility of the afterglow in nitrogen or oxygen.*

6. Two new phenomena are described, namely, *reversed pressure effect* and *reversed temperature effect.* Whereas in an untreated vessel the duration and intensity of the nitrogen afterglow increase (within the pressure limits employed, *ca.* 1.8 mm. to 0.1 mm.) as the pressure is reduced, in a treated vessel a decrease takes place. Similarly, heat markedly decreases the intensity and duration of the afterglow in an untreated vessel, whereas in a treated vessel the duration increases and the intensity is slightly enhanced with heating. These phenomena are explained. A reversed temperature effect is observed in the oxygen afterglow in a treated vessel, the restored glow being weak and of short duration.

7. Paraffin effectively poisons the surface and does not itself catalyze the removal of the active constituents. The intensity, duration and type of decay of the nitrogen and oxygen afterglows are the same in an ordinary as in a paraffin-coated vessel.

8. The decay of the oxygen afterglow is unlike that of the nitrogen afterglow, the former coming to an abrupt termination.

9. Unlike the nitrogen afterglow the oxygen afterglow is not enhanced at the temperature of liquid air. As far as can be observed the oxygen glow is quenched.

MINNEAPOLIS, MINNESOTA

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

ACTIVE NITROGEN. III. THE MUTUAL EFFECT OF NITROGEN AND OXYGEN ON THEIR RESPECTIVE AFTERGLOWS[1,2]

BY BERNARD LEWIS[3]

RECEIVED JULY 21, 1928 PUBLISHED MARCH 6, 1929

Introduction

In the course of an investigation[2b] dealing with the influence of surface on the nitrogen afterglow and the influence of the impurity oxygen in this phenomenon, it was observed that as the pressure of *a* certain mixture of nitrogen and oxygen was decreased, changes occurred not only in the duration and intensity but also in the character of the afterglow. Studies were therefore made with different mixtures of nitrogen and oxygen at various pressures. Among other things the results to be presented will enable one to establish readily any experimental condition desired (within the limits of pressure employed) involving the production of the nitrogen or oxygen afterglow.

It is well known that when oxygen is subjected to the action of an electric discharge, a yellowish-green glow is observed whose spectrum is continuous in character from the reds to the blues.[2c,4] Nitrogen, on the other hand, gives rise to the characteristic orange-yellow afterglow (α-bands).[5] While the nitrogen afterglow lasted longer than four minutes under suitable conditions in these experiments, the maximum duration of afterglow observed in pure oxygen was about thirty-six seconds.

When a mixture of the gases is subjected to the discharge, the type of afterglow one observes is dependent upon the total pressure and the per-

---

[1] Read before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 8, 1928.

[2] (a) Part I, THIS JOURNAL, **50**, 27 (1928); (b) Part II, *ibid.*, 51, 654 (1929). (c) also *Nature*, 121, 938 (1928).

[3] National Research Fellow in Chemistry.

[4] J. J. Thompson, *Phil. Mag.*, 32, 321 (1891); E. P. Lewis, *Ann. Physik*, 2, 459 (1900); R. J. Strutt, *Proc. Phys. Soc.*, 23, 66 (1910) (glow obtained in nitrogen–oxygen mixture); G. Herzberg, *Z. Physik*, 46, 878 (1928); J. Kaplan, *Proc. Nat. Acad. Sci.*, 14, 258 (1928).

[5] E. P. Lewis, ref. 4; *Physik. Z.*, **5**, 546 (1904); R. J. Strutt (Rayleigh), *Proc. Roy. Soc.*, (1911–1916).

centage of the components. For example, consider a gas mixture containing 40% of oxygen and 60% of nitrogen between the limits of pressure employed (ca. 1.8 mm. to 0.01 mm.). As the pressure is decreased the color of the afterglow undergoes the following metamorphoses: yellowish-green, greenish-yellow, blue (several shades), lilac-blue, gradual disappearance of the blue and appearance of the orange-yellow nitrogen afterglow.[6] Indeed, all other conditions being equal, at the same certain total pressure a gas containing 20% of oxygen will exhibit the nitrogen afterglow, whereas a mixture containing 35% of oxygen will show only the oxygen afterglow. It is therefore quite comprehensible that Hagenbach and Frey[7] should have observed the N_2 afterglow in air while Strutt observed only the oxygen afterglow. The apparent contradiction is accounted for by the fact that the observations were made at different pressures; above 0.75 mm. the greenish-yellow glow is in evidence while below 0.3 mm. the orange-yellow glow is prominent. The curves which follow will make this clear.

Apparatus, Material and Method

The electrodeless discharge was employed in order to avoid the contaminating influence of metallic electrodes. The electrical arrangement was the same as described in Part II of this series.2 Conditions as to current, temperature, etc., were maintained as constant as possible. The discharge tube, which was about 20 cm. long and 7 cm. in diameter, was connected in the usual way to a mercury-vapor, high-vacuum pump system and also to a Hyvac oil pump through a small dosing tube. The latter was connected to a bulb and a mercury manometer in which the desired mixture of gases was prepared. Pure oxygen prepared from potassium permanganate and tank nitrogen (containing 0.3% of oxygen by analysis) were used. Each gas was maintained at liquid-air temperature for an hour before making up the mixture. A small amount of the mixed gases was maintained at liquid-air temperature in a trap in the dosing tube before its admittance to the discharge chamber. The lower part of the trap was kept in liquid air throughout a run in order to avoid any possible diffusion of mercury vapor. At each pressure a discharge lasting half a second was passed and several readings of the duration of the afterglow were taken after the cessation of the discharge. Pressures were read on a McLeod gage. Simultaneously, observations were made on the character of the afterglow with a small spectroscope. Readings were made in a completely darkened room. No attempt was made to estimate intensities except in a qualitative manner. The intensity curve follows only approximately the duration curve.

Results

Within the pressure limits employed, a maximum may be observed in the oxygen afterglow down to about 12% of oxygen. With decreasing percentages of oxygen (beginning with pure oxygen) the maximum flattens out and finally diappears and with it also the oxygen afterglow. From 100 to 60% of oxygen only the oxygen afterglow is observed even down

---

[6] In general the same sequence of colors was observed by Constantinides, Phys. *Rev.*, **30**, **95** (1927), as the partial pressure of oxygen was changed. Herzberg (ref. 4) records similar changes.

[7] Hagenbach and Frey, *Physik.* Z., 18, 544 (1917); see also Herzberg, ref. 4.

to very low pressures (*ca.* 0.05 mm.). However, in a mixture containing less than 60% of oxygen, in addition to the above maximum, a sharp minimum is observed (blue afterglow) at a somewhat lower pressure, at which point the intensity and duration become quite small. In the region of this minimum, usually just preceding it, the lilac color begins to appear, which is an indication that the nitrogen a-bands have just become visible. Here the spectroscope shows also the blue continuous background.[8] As the pressure is reduced further, the α-bands become more prominent, the blue portion disappearing, until finally only the former are visible. The nitrogen afterglow rises to a duration maximum at very low pressures (0.035–0.04 mm.).

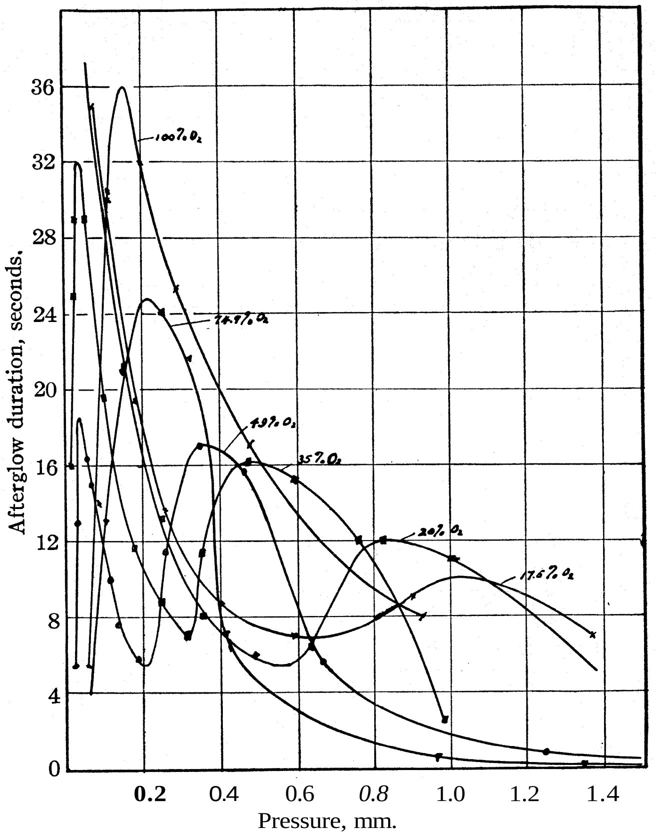


Fig. 1a.

The maximum in the oxygen afterglow, the minimum following it

---

[8] A curious phenomenon was observed in the region of this minimum [*Nature*, 122, 241 (1928)], namely, that entirely different afterglows can be obtained in the same mixture and at the same pressure merely by varying the length of time of discharging.

and the point at which the a-bands are just visible are displaced toward lower total pressures as the percentage of oxygen in the mixture is increased.

The maximum in the nitrogen afterglow duration occurs (within experimental error)[9] at about the same pressure. A few characteristic curves are given in Figs. 1a and 1b to illustrate these points.

If one multiplies the percentage of oxygen by the total gas pressure at the maxima, the minima and the points at which the α-bands appear, constants are obtained. This means that these points always occur at the same partial pressure of oxygen. These oxygen pressures are: maxima, 0.161 mm.; minima, 0.111 mm.; a-bands, 0.123 mm. The following equations, which represent rectangular hyperbolas, are satisfied: $xy = a = 0.161$; $xy = b = 0.111$; $xy = c = 0.123$, in which x is the total gas pressure and y the percentage of oxygen. In Fig. 2 a rectangular hyperbola is

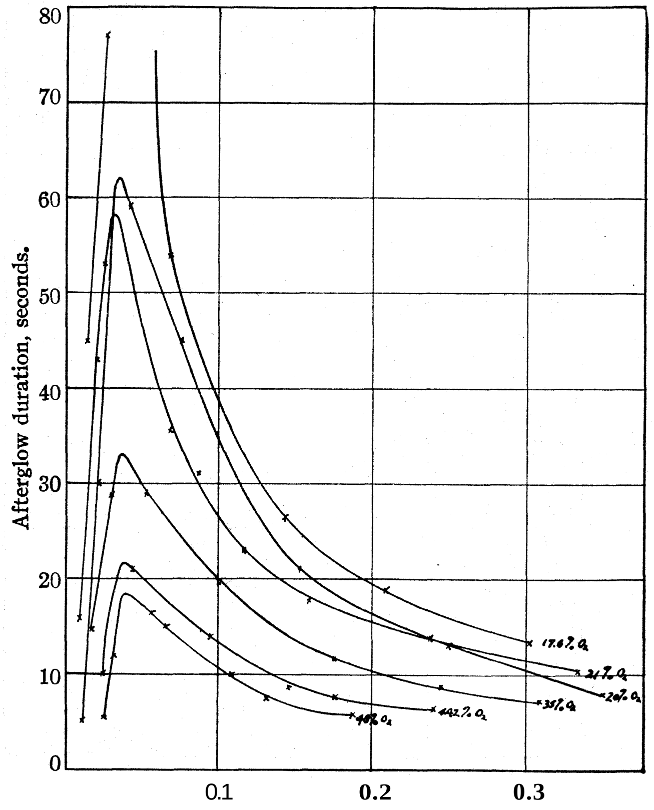


Fig. 1b.

---

[9] Phosphorescence of the glass at lower pressure sometimes prevents an accurate determination of the duration.

plotted for each of these three equations and the experimental points for the maxima, minima and a-bands are laid out on them. The coincidence is **very** good. Another way of emphasizing this is to plot $1/p$ against percentage of oxygen, from which good straight lines are obtained. It is unnecessary, however, to show this. It will be observed (Fig. 2) that for small percentages of oxygen there is a greater divergence between the pressures at which the maxima and minima occur. This means that the maxima should flatten out and become less prominent with decreasing percentage of oxygen. Fig. 1a shows this well. Actually the maxima become so flat as to disappear entirely. Since the oxygen concentration for any set of points is constant, the observed shifts must be due to active nitrogen.

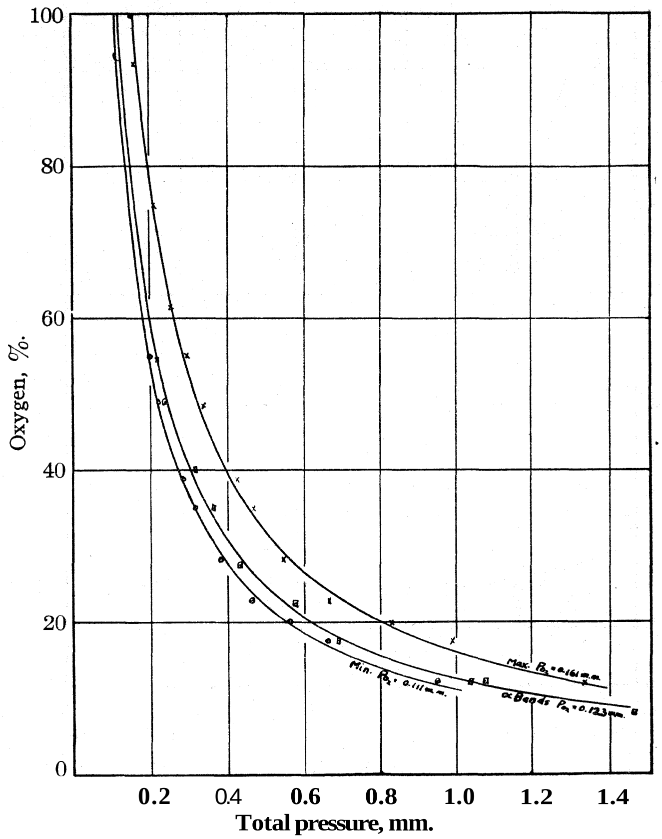
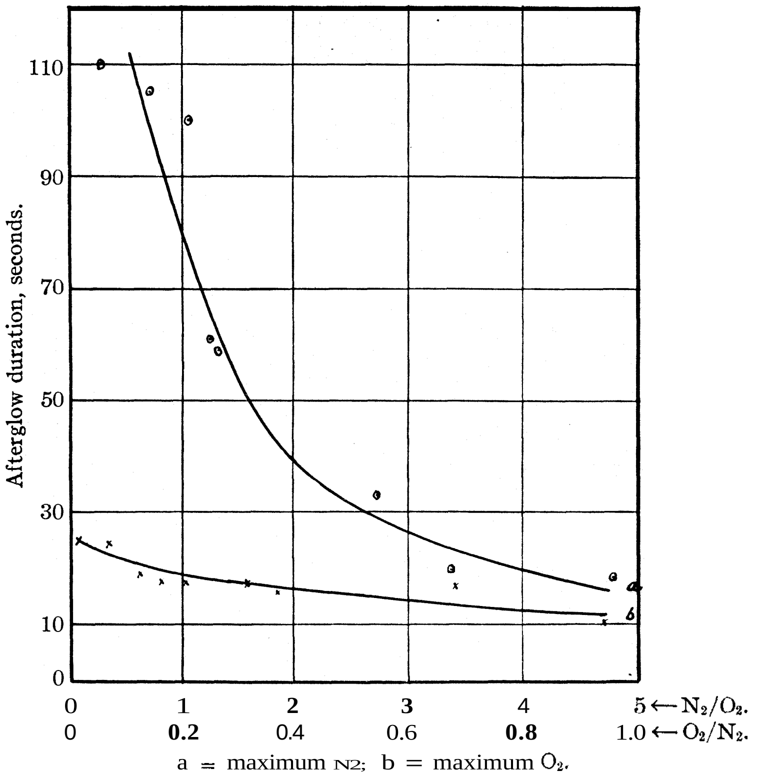


Fig. 2.

In Fig. 3a the duration of the nitrogen afterglow at the maxima is plotted against the ratio of the oxygen concentration to the nitrogen concentration and in 3b the duration of the oxygen afterglow at the maxima is plotted against the ratio of the nitrogen concentration to the oxygen concentration. These curves are only approximately correct since the surface of the discharge chamber was changed after each run by heating and evacuating. It is seen that whereas the influence of oxygen on the nitrogen afterglow is very marked,[10] that of nitrogen on the oxygen afterglow is certainly very slight (the ratio in the latter varied 70-fold). In agreement with this Herzberg* finds that nitrogen led into a stream of glowing oxygen is without



a = maximum N_2; b = maximum O_2.

Fig. 3 (a and b).

effect. It may be concluded that whereas normal oxygen molecules have a marked quenching action on the nitrogen afterglow, normal nitrogen molecules do not affect the oxygen afterglow. Since in these experiments both gases were activated together, the slight quenching action of the oxygen afterglow is probably due to the action of the nitrogen afterglow carriers or active nitrogen molecules or both. It is evident, therefore, that the effect of active nitrogen in quenching the oxygen afterglow is far

---

[10] Compare Constantinides' (ref. 6) and Strutt's (ref. 9) experiments in which a very rapid quenching is observed on passing oxygen into a stream of glowing nitrogen. The amount of quenching is practically proportional to the oxygen concentration.

less than the effect of active oxygen in quenching the nitrogen afterglow. Thus even when the concentration of nitrogen is five times that of oxygen (Pig. 3b), the nitrogen afterglow is effectively quenched, the oxygen afterglow being the only one visible.

Discussion

In presenting the following discussion, the author realizes that no exact formulation of the processes occurring can be attempted at this stage due to the complexity of the system when exposed to the electric discharge. The manifold possibilities are not by any means exhausted in the following list of reactions.

Normal oxygen molecules must be mainly responsible for the quenching of the nitrogen afterglow or, in other words, the removal of nitrogen atoms."" There are several ways in which this could take place

$$N + N + O_2 = N_2 + O_2 + 263{,}000 \text{ cal.}^{11b} \qquad (1)$$
$$N + O_2 + \text{third body} = NO_2 + 124{,}000 \text{ cal.}$$
$$N + O_2 = NO + O + 29{,}000 \text{ cal.} \qquad (2a_2)$$
$$N + NO_2 = N_2 + O_2 + 140{,}000 \text{ cal.} \qquad (2b_1)$$
$$N + NO_2 = 2NO + 97{,}000 \text{ cal.} \qquad (2b_2)$$
$$N + NO = N_2 + O + 72{,}000 \text{ cal.} \qquad (2c)$$
$$N + O + \text{third body} = NO + 191{,}000 \text{ cal.} \qquad (3)$$

No indication is made of excited states of the products.

It is seen that all these reactions are possible from an energy standpoint and it is probable that all of them contribute to the extinction of the nitrogen afterglow. If the product condensed out in liquid air is nitrogen peroxide,[12] it is probable that $2a_1$ contributes to the quenching in a large measure.[13]

[11a] Kaplan and Cario, ***Nature,*** 121, 906 (1928), believe that the excited nitrogen molecule (11th vibrational state in level B) from which the a-bands proceed is brought about by a collision between a metastable nitrogen molecule in level **A** [8 volts] and a metastable N atom (3.56 volts) in which the energy of the latter is transferred to the former. For a discussion of this see H. O. Kneser, *Ann. Physik,* 21, 707 (1928).

[11b] From recent work by H. O. Kneser, [*Ann. Physik,* 21, 707 (1928)] it appears very probable that the mechanism of a-band emission involves a triple collision between two atoms of nitrogen and a third body. The results of his experiments are not in accord with similar results of Bonhoeffer and Kaminsky [Z. ***physik.*** Chem., 127, 385 (1927)], which earlier led them to doubt the triple collision hypothesis. The most recent value for the heat of dissociation of nitrogen is 9.5 volts (or about 218,000 calories) [Gaviola, ***Nature,*** 122, 313 (1928); Birge and Mulliken, 122, Dec. (1928)]. This new value in no way invalidates the theory of Sponer regarding the origin of the a-bands. The process may still be thought of as occurring between a normal nitrogen atom and a metastable nitrogen atom (2.4 volts) in triple collision with a third body.

[12] Majewska and Bernhardt, *Z. Physik,* **48,** 137 (1928). If a discharge is passed through a mixture of the gases, a gas is condensed out at −85° (see Part II). This gas cannot, therefore, be O_3, NO nor N_2O.

[13] There is also, of course, the possibility of formation of NO_2 by the action of O_3 an NO.

It has been mentioned that normal nitrogen-molecules do not affect the oxygen afterglow. Nitrogen atoms could remove oxygen atoms by collision with a third body and thus quench the glow but the concentration of nitrogen atoms is probably too small for this to be marked. It will be assumed for want of evidence as to the intensity distribution in the continuous spectrum in pure oxygen as compared with that in the continuous spectrum in air or in that produced by the oxidation of nitric oxide by ozone, that the oxygen afterglow is due to the emission of radiation (see Thompson, ref. 4) when two oxygen atoms, possessing any velocity, combine. This may occur in a two body collision,[14] so that competition for the reactions N + O + third body and O + O is in favor of the latter. The small quenching effect of the oxygen afterglow by active nitrogen may easily be due to the active nitrogen molecular species.

It would be valuable from the standpoint of atomic kinetics to make calculations at the minima, where the a-bands appear, of the collisions between the various species present in the glowing gas, to determine if possible at what concentration of atomic nitrogen the a-bands become visible. In view of the complicated system of reactions which may be occurring, the uncertainties involved in the fractions of oxygen and nitrogen which are dissociated by the discharge and the fruitfulness of such collisions as between two nitrogen atoms, it is doubtful whether the calculation would have much meaning. One may simplify the problem by considering only the reactions $2a_1$ and $N + N = N_2' \longrightarrow$ a-bands. In a mixture containing 20% of oxygen, the minimum occurs at 0.56 mm. Assuming 1% dissociation of nitrogen, which may be high,[15] and disregarding dissociation of oxygen, we find the number of collisions between N and O_2 ($\sigma_N = 1.77$ Å. and $\sigma_{O_2} = 1.44$ Å.) equal to 2.77×10^{20} per cc. per sec. Since this requires the intervention of a third body and the ratio of triple to double collisions is[16] about $^1/_{1000}$, this becomes roughly 3×10^{17} collisions per cc. per sec. The number of collisions between N and N is 1.7×10^{19} per cc. per sec. This calculation shows at least that such an encounter as between two nitrogen atoms results in a molecule very infrequently, for otherwise it would be possible to see the a-bands at a much higher pressure than corresponds to the minimum. One arrives at the same result from classical theory. It is believed that only atoms possessing certain velocities can combine.[17] In fact the temperature coefficient of the

---

[14] Oxygen has a continuous absorption spectrum beginning at λ1751 and can emit continuously by electron transition.

[15] Crew and Hulbert, *Phys. Rev.*, 30, 124 (1927).

[16] At atmospheric pressure, Herzfeld, *Z. Physik*, 8, 132 (1921).

[17] Indeed, the persistence of the oxygen afterglow even in the presence of "active" nitrogen at pressures of nitrogen many times that of oxygen, is probably due to the ease with which two oxygen atoms combine as compared with the combination of two nitrogen atoms.

nitrogen afterglow (between room temperature and liquid air temperature) can be accounted for if one assumes that only atoms combine which possess velocities below some small critical value. Since the a-bands just become visible in the region of the minimum it is evident that a sufficient number of these fruitful collisions are taking place. These must increase in number as the pressure is reduced, for the intensity of the a-bands increases. In a general way this can be understood, for the fraction of nitrogen molecules dissociated by the discharge increases as the pressure is reduced[15,18] and the number of suitable collisions between N and N must therefore increase faster than deactivating collisions.

I am indebted and thankful to Professor S. C. Lind for his constant interest and advice during the tenure of this Fellowship and for placing at my disposal the facilities of his laboratories.

Summary and Conclusions

A study is made with the electrodeless discharge of the nitrogen and oxygen afterglows in mixtures of nitrogen and oxygen at various pressures. A sequence of changes in the character of the afterglow is recorded as the pressure is reduced in the same mixture This may' be divided roughly between the oxygen afterglow at higher pressures and the nitrogen afterglow at lower pressures with a maximum in each and a minimum between the two. Within the limits of pressure employed (*ca.* **1.8** mm. to **0.01** mm.) and from **100** to **60%** of oxygen, only the oxygen afterglow with its maximum is observed. At lower percentages of oxygen the minimum appears and also the nitrogen afterglow. Below about 12% of oxygen, the oxygen afterglow maximum disappears and with it also the oxygen afterglow. The α-bands just become visible at a total pressure slightly higher than that at the minimum.

The oxygen maxima, the minima and the points at which the a-bands just appear are displaced toward lower total pressures as the percentage of oxygen increases. It is found that these points always occur at a constant partial pressure of oxygen: oxygen maxima, **0.161** mm.; minima, **0.111** mm.; a-bands, **0.123** mm. The experimental points fit the corresponding hyperbolas very well. The nitrogen afterglow rises to a duration maximum at a pressure of about 0.035–0.04 mm. *The curves and data presented enable one to determine any experimental condition desired (within the pressure limits employed) involving the production of the nitrogen or oxygen afterglows.*

It is concluded that normal oxygen molecules have a marked quenching action on the nitrogen afterglow but that normal nitrogen molecules have no effect on the oxygen afterglow. The slight quenching action in the oxygen afterglow is probably due to active nitrogen molecules.

[18] This is also evident from the fact that with decreasing pressure in either pure nitrogen or oxygen the glow becomes more intense and of longer duration.

Calculations show that the fruitfulness of collisions between two nitrogen atoms to form a molecule is small. The temperature coefficient of the afterglow in nitrogen can be explained on the basis that only atoms possessing velocities below some critical value can combine on colliding.

MINNEAPOLIS, MINNESOTA
BERLIN, GERMANY

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. VI

BY G. L. MATHESON AND O. MAASS

RECEIVED AUGUST 6, 1928 PUBLISHED MARCH 6, 1929

The following paper is one of a series[1] that deals with the properties of pure hydrogen peroxide. In it several new freezing-point curves are described and the existence of compounds between hydrogen peroxide and a number of organic bases is investigated. The measurements of the heat of decomposition, the molecular weight in the vapor phase and the explosion temperature of pure hydrogen peroxide are described.

Pure hydrogen peroxide was prepared in much the same manner as was set forth in the first paper of this series with a few slight modifications. The concentration, by evaporation in *vacuo*, was carried out until the strength was about 98% by weight. The distillate produced in the final stages of evaporation was saved. The final purification was carried out as before by means of fractional crystallization.

Freezing-Point Curves.—This section of the experimental work deals with the solubility and freezing-point curves of various substances in pure hydrogen peroxide. These experiments are of interest in comparison with corresponding water systems. The apparatus employed consisted of a long test-tube set in a bath of ether in a transparent Dewar flask. A stirrer was provided in the tube and the bath was stirred by bubbling air through it. Its temperature could be controlled by adding carbon dioxide snow or by changing the rate of flow of air. The temperature was measured by a thermometer placed in the bath. The materials were added in the most convenient manner for each substance. The chemicals used were all carefully purified to remove foreign substances which might decompose the peroxide. The temperatures are those recorded just as the last crystals disappeared when the bath was slowly warmed.

In Table I the results are recorded for potassium chloride, sodium fluoride, potassium sulfate and methyl alcohol, and these systems are plotted in Figs. 1 and 2, with the corresponding water systems.

The data for the water curves are taken from the literature with the exception of the one for sodium fluoride, for which the following points

---

[1] Maass and Hatcher, THIS JOURNAL, 42, 2548 (1920).

TABLE I

FREEZING POINTS IN HYDROGEN PEROXIDE

Potassium Chloride	
Mole %	M. p., °C.
2.0	− 3.4 H_2O_2 solid phase
4.8	− 6.5
7.1	−10.4
9.4	−14.6
11.9	−20.2
13.9	−25.0
15.9	−31.4
17.0	−24.2 KCl solid phase
18.7	−16.0
20.5	− 7.0
22.1	− 1.0

Sodium Fluoride	
3.8	− 5.2 H_2O_2 solid phase
7.4	− 9.1
8.6	−10.6
9.8	−12.1
11.1	−13.9
12.3	−15.2 Eutectic

Potassium Sulfate	
Mole %	M. p. °C.
0.87	− 2.0 H_2O_2 solid phase
2.27	− 4.8
3.68	− 8.2
5.3	−12.3
7.6	−17.5
8.4	−23.5
14.1	−11.0 K_2SO_4 in solid phase
15.9	+ 0.5

Methyl Alcohol	
5.6	− 1.7 H_2O_2 solid phase
13.2	− 6.4
18.4	−10.2
25.2	−15.3
28.3	−18.6
33.2	− 222
43.8	−37.8
51.5	−49.3

were determined by the authors: 0.6%, −1.1° and 1.03%, −1.9° with ice as the solid phase. The eutectic was found to be at −2.9° for a per-

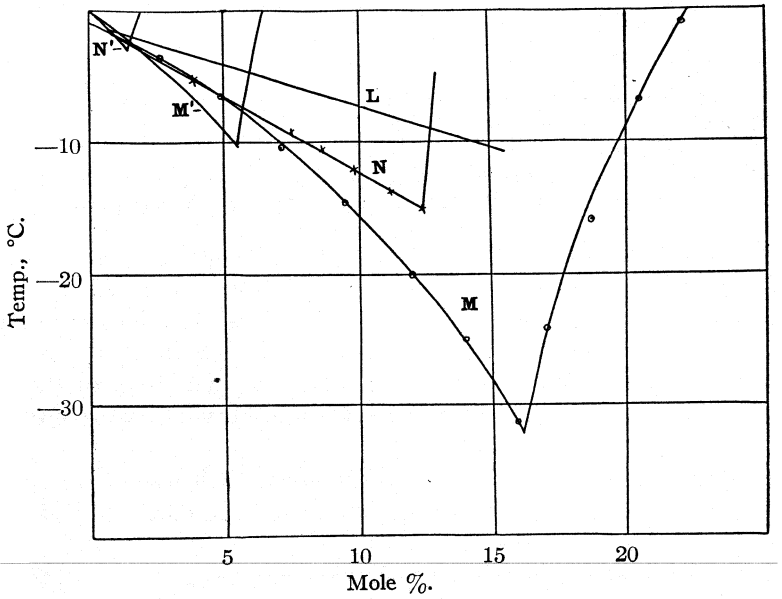
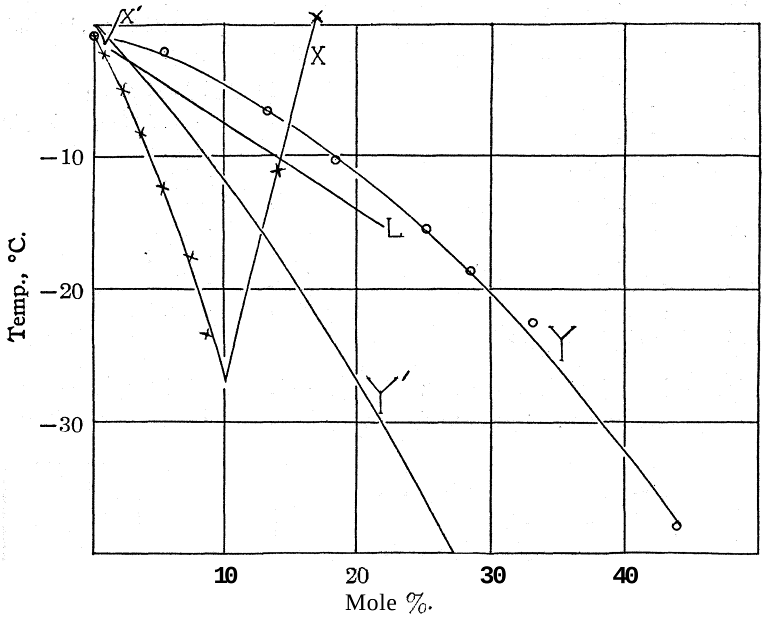


Fig. 1.—Freezing-point curves. L, Theoretical lowering in H_2O_2; M, H_2O_2–KCl; M', H_2O–KCl; N, H_2O_2–NaF; N', H_2O–NaF.

centage of 1.4. —5.6" was obtained by Guthrie as the eutectic,[2] but the authors found that the solution froze to a solid if cooled below −2.9°. The straight line L, plotted in each figure, represents the theoretical lowering of the freezing point in hydrogen peroxide caused by a substance which does not ionize or associate when dissolved.

In the potassium sulfate system no points could be recorded between the concentrations of 8.4 and 14.1% because the liquid froze to a glass. The same difficulty was encountered with methyl alcohol beyond 51.5%.



Pig. 2.—Freezing-point curves. L, theoretical lowering in H_2O_2; X, H_2O_2–K_2SO_4; X', H_2O–K_2SO_4; Y, H_2O_2–CH_3OH; Y', H_2O–CH_3OH.

From the figures it is apparent that the salts are dissociated in pure hydrogen peroxide whereas methyl alcohol is associated, all of which is indicated by the relative angles of the L curves and the freezing-point curves at infinite dilution. In every case, the eutectic in the hydrogen peroxide system occurs at a far higher concentration than in the corresponding water system, indicating a greater solubility in hydrogen peroxide than in water.

Potassium bromide was found to decompose hydrogen peroxide fairly rapidly, no matter how many times the salt had been purified by recrystallization.

When ether is added to hydrogen peroxide only a slight amount dissolves before a separate layer is formed. The peroxide is fairly soluble in this

---

[2] Guthrie, *Phil, Mag.*, 5, 640 (1878).

second layer, a considerable amount of heat being evolved during its solution. Freezing points which were obtained for the ether–hydrogen peroxide system are contained in Table II.

TABLE II

FREEZING POINTS IN HYDROGEN PEROXIDE

Ethyl Ether

Weight, %	M. p., °C.	Weight, %	M. p., °C.
3.5	−1.2 (Two distinct layers)	47.8	− 6.0
41.6	. . . H_2O_2 layer nearly gone	59.2	−16.5
44.3	−4.8	66.5	−33.1
45.2	−5.1	71.5	−47.6

As long as there were two layers present, the freezing point of the lower layer was −1.2°. The freezing point of pure hydrogen peroxide is −0.9°,[3] that is, within 0.3° of the freezing point of the peroxide layer. Since the latter determination may be 0.2" too low on the absolute scale, the lower layer must have consisted of well-nigh pure peroxide. This shows that only a very slight amount of ether is soluble in pure hydrogen peroxide. When the peroxide layer had just disappeared the freezing point was still very high and the solid which crystallized out was filtered off at a low temperature and analyzed. The composition of the solid varied from 51.7% by weight of hydrogen peroxide to 45%, depending on the concentration of the solution. The composition of the ether layer varied with change of temperature when there were two layers in equilibrium, being 60.8% by weight of hydrogen peroxide at 0° and 64% at 20°, with complete miscibility somewhere in the neighborhood of 80°. The solid which is formed on cooling an ether solution may be a solid solution. The complete phase rule diagram is probably similar to that of succinic nitrile and water.

The system sulfuric acid–hydrogen peroxide was examined and where possible the freezing points were determined. The most convenient way of introducing definite quantities of anhydrous sulfuric acid was to add gaseous sulfur dioxide, which united with the peroxide, even when very cold, to form sulfuric acid. Table III contains the data thus obtained.

TABLE III

FREEZING POINTS IN HYDROGEN PEROXIDE

SO_2, mole %	5.8	11.7	13.9	19.5	47.2	48.4	49.7	50.5
M. p., °C.	−5.3	−11.5	−18.0	−31.0	−10.0	−3.3	+2.4	+4.1

The solution was very viscous between 19.5 and 47.2% of sulfur dioxide and no crystals were obtainable. Between these percentages the solution solidified to a glass when the temperature was lowered below 25". Toward the end of the addition a slight decomposition was noticed with the formation of ozone. This accounts for the lowering of the freezing point

---

[3] Cuthbertson, Matheson and Maass, THIS JOURNAL, 50, 1120 (1928).

of the sulfuric acid formed, since at 50% sulfur dioxide the freezing point should have been 10°, that of pure sulfuric acid. The two portions of the curve obtained indicate that more than one eutectic is formed. This would show that some compound between sulfuric acid and hydrogen peroxide is formed. The great tendency to supercool prevented the isolation of crystals.

An apparatus has been described in a previous paper[4] for the examination of the ammonia–hydrogen peroxide system. An attempt was made to use this apparatus for the similar system phosphine–hydrogen peroxide. Great care was taken in the purification of the phosphine. It was found, however, that even in supercooled peroxide phosphine was soluble to an exceedingly slight extent.

The fact that ammonia formed a stable compound with the peroxide, whereas phosphine did not, seemed to indicate that the more basic the substance, the more readily would it combine with peroxide to form a stable compound. With this in view, the effect of a large number of organic bases was tried. It was found that the peroxide remained stable and the amine unoxidized when in contact at low temperatures, that is, below 0°. If the solutions were allowed to warm up to room temperature

TABLE IV

FREEZING POINTS IN HYDROGEN PEROXIDE

Mole %	M p., °C.	Mole %	M. p., °C.	Mole %	M p., °C.	Mole %	M. p., °C.
Piperidine		39.6	− 9	13.3	−10.5	Di-*iso*butylamine	
5.6	−10.3	43.5	−11	166	− 3	2.24	− 2.5
11.1	−32.5	46.3	−13	21.9	+15.5	5.75	− 8.5
12.4	−43.0	51.4	−19	24.2	4-21	8.5	−17
		56.0	−23	27.7	+25	10.9	−30
Diethylamine		59.5	−18	28.2	+24		
3.05	− 8.4	62.7	−12	31.2	+26	Tripropylamine	
11.3	−35.0	65.4	− 9.5	34.5	+23	3.0	− 4
		69.7	− 9	36 8	+20	9.1	−14.5
Mono-n-butylamine		71.4	−11	38.7	+16.5	12.1	−30
129	− 2 7	73.0	−13	39.9	+17		
4.61	− 9.0	75.8	−16.5	49.9	+17	Dimethylaniline	
8.37	−14 0	77.9	−20.5	53.1	+15.4	6.35	− 2.3
12.5	−29.0			55.5	+13.5	12.17	− 3.0
16.7	Froze to glass	*Tert.*-monobutylamine		58.5	+10	When warmed oil separated	
				60.8	+ 7		
20.7	Froze to glass	1.69	− 2	63.0	+ 8	Further addition gave two layers	
		3.82	− 5	65.0	+ 7.3		
23.0	0	5.47	− 7.5	66.6	+ 5.5		
24.0	− 2	8.40	−15	59.3	+ 5.0		
27.2	−10	9.22	−18	72.2	+ 1.5		
30.0	−10	12.7	−12	74.4	− 0.5		
33.6	− 8			76.4	− 5.0		

---

[4] Maass and Hatcher, THIS JOURNAL, 44, 2473 (1922).

some of the amines caused decomposition of the peroxide, with oxidation of the amine to the nitro compound. Piperidine was the most active in producing decomposition, and when warmed to room temperature the heat of the reaction was sufficient to accelerate it progressively until the peroxide decomposed with explosive violence. The monobutylamine with the tertiary carbon atom attached to the nitrogen was the most stable of the amines tried, no decomposition taking place. The *iso*-normal-butylamine was next in the order of stability. In a test with the latter, less than 1% of peroxide decomposed after being in contact with various concentrations of this amine for eight hours, at temperatures below 0°.

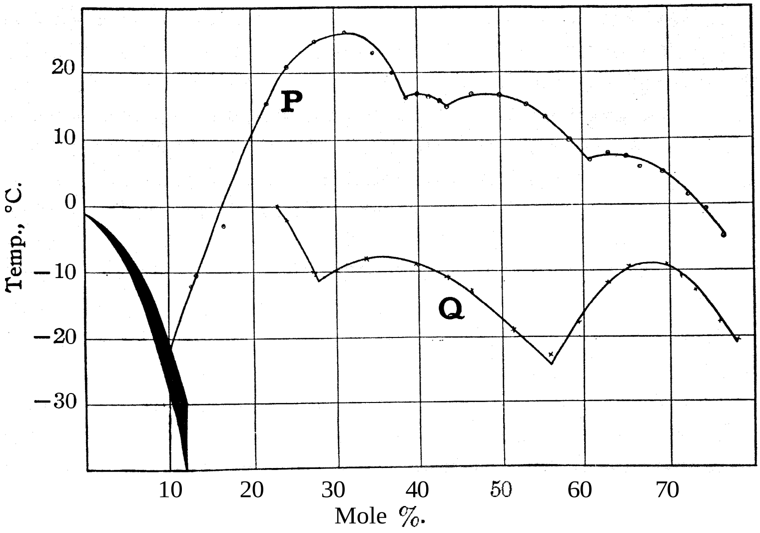


Fig. 3.—Freezing-point curves. Q, Mono *N*-butylamine–hydrogen peroxide. P, Mono butylamine–hydrogen peroxide.

In Table IV are given the freezing-point determinations made with the organic bases and hydrogen peroxide. Only in the case of the isomeric monobutylamines, the normal and tertiary, could a large part of the freezing-point curve be determined. In the case of all the others, no crystals could be formed at the higher concentrations of the organic base, since the mixture froze to a glass once the first eutectic had been passed.

Figure 3 represents all the points given in the above table. The depression of the freezing point of the peroxide was the same for all the bases, within experimental error, with the exception of the dimethylaniline. To prevent confusion the line is broadened to include all these points. In the case of the monobutylamine stable compounds were isolated. The compound having the composition $2H_2O_2 \cdot C_4H_9NH_2$ was obviously the most stable. In the case of the n-butylamine a compound of the same molecular proportions was also isolated, with the indication, also, of a compound containing a greater proportion of hydrogen peroxide. As is well known this amine is oxidized to hydroxylamine at higher temperatures in aqueous solutions. This again illustrates the hypothesis that a molecular compound is generally formed between two substances before reacting and subsequent splitting up. Dimethylaniline, the only benzenoid amine investigated, behaved quite differently compared with the aliphatic amines. It was not as soluble in the peroxide and the small lowering of the freezing point of the peroxide indicated that it was associated in solution.

As it was not improbable that the other amines formed compounds which could not be crystallized out, due to supercooling, an entirely different method was resorted to in an attempt to isolate such compounds. This depended on the precipitation of an oil, from a mixture of anhydrous ether solutions of the amine and the hydrogen peroxide, with subsequent analysis of the resulting oil. This method had been found successful in the isolation of the ammonia compound.[4] The following will illustrate the procedure. When small portions of an ether solution of, for instance, diethylamine, were added to an ether solution of peroxide, successively, with vigorous stirring, at first an oil kept separating out. With further addition of amine this oil went back into solution. It was found that ether was not soluble in this oil, any more than in pure peroxide (see above). Hydrogen peroxide was soluble in the oil and could only be washed out by ether with great difficulty. Amine was also soluble in the oil but its far greater solubility in ether made it relatively easy to wash out the excess amine from the oil by means of anhydrous ether. The amine solution was therefore added until the maximum amount of oil had been precipitated and a slight amount more of amine was added, as indicated by the partial redissolving of the oil. The remaining oil was separated and could then be washed with ether. It was found that the composition of the oil was invariable, independent of the number of washings it had received. Furthermore, the analysis of the oil, in the case of all the amines tried, gave an exact molecular proportion of amine to peroxide.

Permanganate could not be used for titrating the peroxide in the presence of the organic bases. Hence the method used to analyze the oil was to dissolve a weighed portion of it in water and then add powdered manganese dioxide. The peroxide decomposed completely within a minute and the oxygen evolved was then measured.

Dimethylaniline, aniline, pyridine, phenylhydrazine, tripropylamine and di-isobutylamine did not give insoluble oils in ether. It cannot be taken for granted that because an oil does not separate on mixing ether solutions of organic bases and peroxide that no molecular compounds are formed. It was found that the more carbon atoms there were, to the amine, the greater was the solubility of the resulting oil in the ether; in the case of certain amines great care had to be taken to use concentrated ether solutions in order to get any oil at all. It seems probable, however, that some of the above bases do not form compounds with the peroxide. For example, dimethylaniline indicated this by its relative insolubility in the peroxide.

In Table V are given the results of the analyses of the oils that were formed, the percentages found and calculated being given in weight percentage of hydrogen peroxide. The exact agreement between the percentages found and calculated leaves little doubt as to the existence of these molecular compounds.

TABLE V

COMPOSITION OF OIL SEPARATING FROM ETHER

Base	Weight of H_2O_2 Found	Weight of H_2O_2 Calcd.	Compound
Ammonia	66.7	66.7	$NH_3 \cdot H_2O_2$
Ethylamine	59.5	60.2	$2H_2O_2 \cdot C_2H_5NH_2$
n-Propylamine	53.2	53.7	$2H_2O_2 \cdot C_3H_7NH_2$
Isobutylamine	48.7	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
n-Butylamine	48.5	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
Tert.-monobutylamine	48.3	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
Diethylamine	58.0	58.3	$3H_2O_2 \cdot (C_2H_5)_2NH$
Triethylamine	58.3	57.5	$4H_2O_2 \cdot (C_2H_5)_3N$
Piperidine	44.2	44.4	$2H_2O_2 \cdot C_5H_{10}NH$

Monobutylamine gave an oil which could be solidified at will, and having the same composition and freezing point as the stable compound indicated by the freezing-point curve. The same could be done in the ease of the ammonia. All this indicates that the above method gives a reliable means of isolating those compounds which cannot be separated in the crystal form.

A feature of interest in the above table is the increase in the number of peroxide molecules taken up by the ethylamines with increase in substitution of the nitrogen hydrogens by ethyl groups. As a general conclusion, the possibility of forming a stable compound depends on the basicity of the base.

Heat of Decomposition of Hydrogen Peroxide

The heat of decomposition of hydrogen peroxide into water and oxygen was measured in an adiabatic calorimeter. The decomposition apparatus is shown in Fig. 4. It consisted essentially of two bulbs, A and B, which were joined by means of a ground-glass joint. This apparatus was submerged in the calorimeter water, leaving the two thin-walled glass tubes C and D protruding from the surface. Bulb A was filled with lumps of manganese dioxide which served to decompose any hydrogen peroxide carried over by entrainment. A quantity of peroxide was allowed to flow through a capillary funnel passing through Tube D into Bulb B. The amount which entered in this way was determined by weighing B before and after filling. A rubber tube was attached to C and led to a U-tube filled with pumice stone and sulfuric acid, outside of the calorimeter proper. The object of this was to catch any water vaporized during the decomposition and carried away with the oxygen, and thus to be able to correct for the heat of vaporization of this water. Actually it was found that this correction was very small, since, apparently, most of the water vapor with which the oxygen was saturated was reabsorbed in Bulb A.

After the apparatus had been put together, the calorimeter was brought to thermal equilibrium. The decomposition of the peroxide was started by dropping a small grain of manganese dioxide down Tube D, which was then immediately closed to force the oxygen along the other tubing. Most of the heat given off was transmitted through the walls of Bulb B, directly, from the liquid peroxide. The rate of reaction was controlled by the proper choice of the size of the initial grain of manganese dioxide. Toward the end, when the reaction slowed up, more manganese dioxide was added to increase the rate of decomposition. It was found that the reaction came to an abrupt end, as indicated by the sudden cessation of temperature change in the calorimeter. Throughout the whole process great care was taken to have complete adiabatic control. A sample calculation below gives an idea of the accuracy with which the determinations were made.

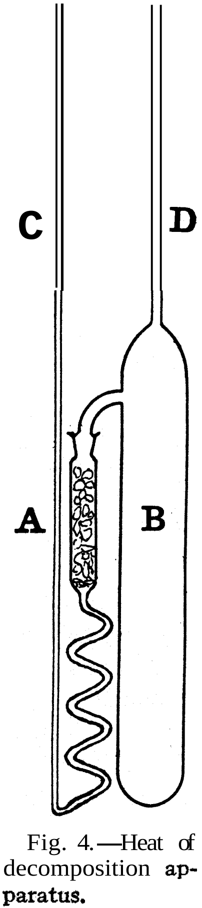


Fig. 4.—Heat of decomposition apparatus.

Sample Calculation

Concentration of peroxide = 38.05%
Weight of calorimeter + water = 1272.8 g.
Weight of calorimeter = 269.6 g.

Weight of water = 1003.2 g.

Water vapor carried out by oxygen
Weight of U-tube + water = 46.7191 g.
Weight of U-tube = 46.7176 g.

Weight of water vapor = 0.0015 g.

Weight of peroxide
Weight of Bulb B + H_2O_2 = 27.236 g.
Weight of Bulb B = 17.275 g.

Weight of H_2O_2 = 9.961 g.

Temperature change of calorimeter
Final reading = 3.784°
Initial reading = 1.345°

Change = 2.439'

The water equivalent of the calorimeter was made up as follows.

21.26 g. of glass: sp. ht. taken as 0.17 cal. Water equivalent = 3.62 cal.
9.38 g. of MnO_2: sp. ht. calculated from the atomic heats. Water equivalent = 1.16 cal.
298.2 g. of copper calorimeter and stirrer. Water equivalent = 24.70 cal.
Total water equivalent = 29.5 cal.

Heat change in water = 2444.4 cal.
Heat change in apparatus = 72.0 cal.
Heat carried off by water vapor = 0 9 cal.
Heat of residual water left in Bulb B = 19.8 cal
Total calories = 2537.1

Molecular heat of decomposition at 20° and concentration of 38.05% is

$$\frac{2537.1 \times 34.01 \times 100}{9.961 \times 38.05} = 22{,}714 \text{ cal.}$$

The heat of the reaction at 20° as represented by

$$H_2O_2(\text{liq.}) = H_2O(\text{liq.}) + \frac{1}{2}O_2(\text{ gas at atmos. press.}) + \text{Heat}$$

was found to be as follows. Two determinations of 97.15% peroxide gave 23,400 and 23,440 cal., respectively. Two determinations of 38.05% peroxide gave 22,746 and 22,714 cal., respectively. The heat of dilution between the above percentages is 690 cal. per mole, and the heat of decomposition of pure hydrogen peroxide averages 23,450 cal., which is considerably higher than values found in the literature.

The Molecular Weight of Hydrogen Peroxide in the Vapor State

The molecular weight of hydrogen peroxide in the vapor phase is difficult to determine because of its rapid decomposition at temperatures which would give measurable vapor pressures. A recent determination of the vapor pressure curve for pure hydrogen peroxide[5] indicated that such an experiment might, however, be carried out with success if the temperature was about 90°. At this temperature the vapor pressure of peroxide is about seven centimeters.

The apparatus used to carry out the experiment was of the Victor Meyer type. It is shown in Fig. 5. It consisted essentially of a large flask C with a long neck. It had a capacity of about 2400 cc. and the neck was 60 cm. long. The flask was sunk in the water-bath I, which was stirred by the paddles N. The connecting tubing E was heated by means of nichrome wire embedded in asbestos. The current was regulated so that the temperature was about 5° above the bath temperature. A small tube F, filled with a few lumps of manganese dioxide, was inserted next to the manometer M. This served to protect it from the peroxide. A and B

---

[5] Maass and Hubert, THIS JOURNAL, 46,2693 (1924).

were outlets to a hydrogen reservoir and a vacuum pump, respectively. The magnetic device K for dropping the capsules of peroxide was fitted to the apparatus by means of a ground-glass joint.

The apparatus was made of pyrex glass but even so peroxide decomposed rapidly in it. It was found that if the glass surface was coated with a thin film of beeswax the decomposition was greatly reduced.

The procedure employed in using the apparatus was as follows. The bath was heated to 92° and at the same time the apparatus was thoroughly evacuated. Then it was filled to atmospheric pressure with dry hydrogen. The capsule with a weighed amount of pure hydrogen peroxide was inserted in the magnetic dropping device. This part of the apparatus was kept cool by blowing a current of air across it when the peroxide capsule was in it. The capsule was made of beeswax. A few drops of peroxide were poured into it and by difference in weight the amount of peroxide was known. The mouth of the capsule was closed after weighing until only a very fine opening was left. This was necessary to allow the air to escape when the pressure was reduced in order not to burst the capsule. When the capsule was in place the pressure was quickly lowered to one centimeter. At this pressure and room temperature the pure peroxide in the capsule was still far from its boiling point and not much could be lost by evaporation through the fine hole in the capsule. When the pressure had been reduced, two or three successive readings were taken on the manometer and then the capsule was dropped to the bottom of the flask C where the wax of the capsule melted and the peroxide was free to vaporize. Pressure readings were then taken at known intervals of time. At the same time the barometric pressure was observed in order to make corrections for its change. The object of the presence of the hydrogen gas was, of course, to prevent peroxide vapor from reaching the manometer. The dimensions of the flask and the narrow tube connections were chosen in order to reduce diffusion through the hydrogen as much as possible.

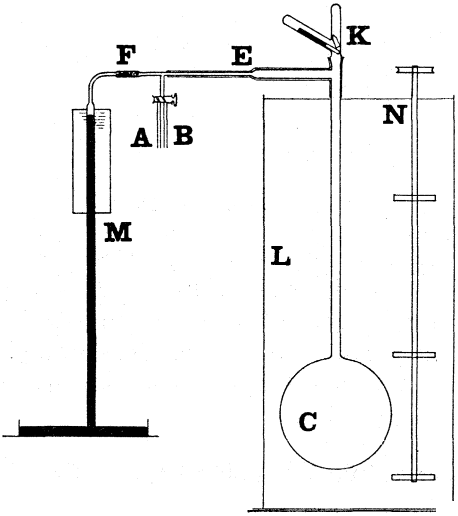


Fig. 5.—Vapor density apparatus.

The results obtained are given in the next table, VI, and plotted in Fig. 6. Experiment E was made with 56.6% peroxide instead of 100%, as in the case of the others.

TABLE VI

INCREASE IN PRESSURE (CM.) WITH TIME (MIN.)

Experiment	A	B	C	D	E
Weight of H_2O_2, g.	0.0774	0.0631	0.1052	0.0196	0.0468 (56.6%)
Temp., °C.	92	92	92	92	92
Time, min.			Pressure, cm.		
1	1.15	0.8	1.87	0.46	1.52
2	1.64	1.48	2.64	.52	1.74
3	2.00	1.74	2.96	.56	1.76
4	2.15	1.78	3.03	.57	1.77
5	..	1.79	3.07	.57	1.79
6	2.24	1.80	3.11	.57	1.81
7	2.25	1.82	3.13	.57	1.81
8	2.26	1.83	3.11	.57	1.81
9	2.29	1.84	3.13	.57	1.81
10	2.30	1.85	3.16	..	1.81
11	2.31	1.86	3.17	..	..
12	2.33	..	3.18	..	..
13	..	..	3.20	..	..
14	2.35	..	..	.60	..
16	2.38	1.90	..	..	..
18	2.42	..	3.28	..	..
19	..	..	..	.62	..
21	..	1.95	..	..	..
23	..	..	3.35	..	..
24	..	..	..	.64	..
28	..	..	3.40	..	..
29	..	..	..	.66	..
33	..	..	3.45	..	..
34	..	..	..	.68	..

A question that at once arose from the above curves was what portion was to be taken as the final pressure due to hydrogen peroxide vapor only. The answer for curves D and E, where only a small quantity of peroxide was used, was obviously the constant pressure portion. It seemed apparent from curve D that the action consisted, first, of a boiling of the peroxide to form a vapor and then a diffusion upward to the unwaxed portion of the system, the magnetic dropping device, where the peroxide decomposed. When a much larger quantity of peroxide was used the decomposition started before the boiling had finished and no constant pressure was reached. It did not appear correct, therefore, to extrapolate back to zero time and take that pressure as the correct one because the decomposition did not set in at the start. If six minutes from the start was taken as the point where evaporation ceased and decomposition just started, then the molecular weight determinations were as follows: A = **34.0; B** = **34.3;** *C* = **33.9;** D = **34.0;** mean = **34.0.** Thus the molecular weight of hydrogen peroxide in the vapor phase is **34.**

If, on the other hand, the molecular weight is determined by extrapolation of the decomposition curve back to zero time, then the values are: A = 34.9; B = 34.5; C = 34.4; D = 35.2. From what has been said above these values are too high.

In Experiment E, in which 56.6% peroxide was used, the pressure was calculated which would be obtained if 34 were taken as the molecular weight of the peroxide and this pressure was compared with that observed. The observed pressure was $1^1/_3\%$ less than the theoretical. Experiments were carried out with water, under identical conditions of pressure and temperature, to check the apparatus. These gave molecular weights of slightly under 18.1.

The above experiments with peroxide have been repeated many times with the same conclusion that, like water vapor, it is unassociated in the vapor state.

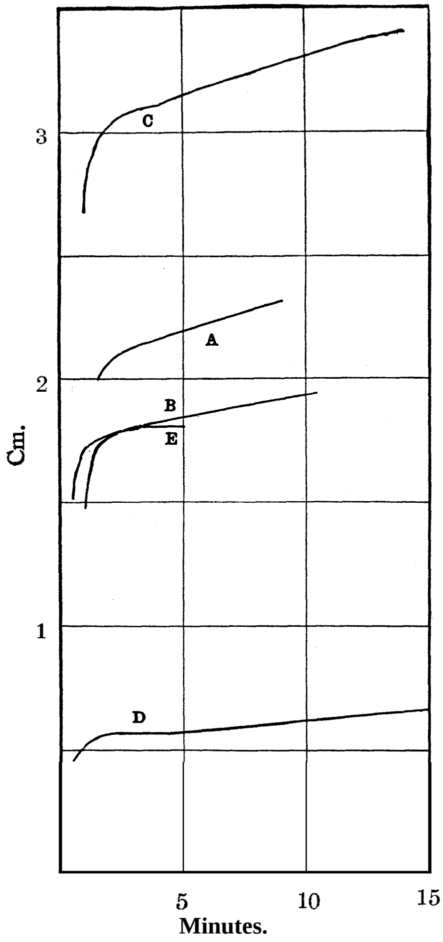


Fig. 6.—Increase of pressure with time.

The Explosion Temperature of Pure Hydrogen Peroxide

The minimum temperature of decomposition of hydrogen peroxide where the rate would be classed as explosive was investigated for a certain set of conditions. In these experiments the decomposition was called explosive when it made an audible report or "bang." The method of procedure was to drop about 0.05 to 0.3 g. of pure peroxide contained in a paraffin capsule into a tube about three centimeters in diameter. This tube was placed vertically in a deep oil-bath. The temperature of the oil-bath was taken with a mercury thermometer totally immersed in it. The results, which could be repeated every time quite independently of the quantity of peroxide used, were as follows: 146°, no explosion; 150°, dull explosion, barely audible; 151°, fairly sharp explosion; 153°, violent explosion; 159°, violent explosion of about the same intensity as at 153°.

The experiments were repeated with a saturated solution of potassium chloride in pure peroxide: 151°, no explosion; 160°, rapid decomposition to give a flame but no audible explosion.

At 160" a 95% solution of peroxide and water gave the same result as the potassium chloride solution at the same temperature.

From the results with the pure peroxide the nature of the explosion was seen to change rapidly between 150 and 153°. This indicates that the pure hydrogen peroxide explodes when it is heated to its boiling point. Dissolved potassium chloride or water, if anything, raise the explosion temperature.

Acknowledgment is made to the Research Council of Canada for a Studentship awarded to one of us during the period in which the work was carried out.

Summary

Melting-point curves were determined in pure hydrogen peroxide and a comparison was made with the analogous curves in water for potassium chloride, potassium sulfate, sodium fluoride and methyl alcohol. Curves were also obtained for ethyl ether and sulfuric acid in hydrogen peroxide.

Melting-point curves of *n*-butylamine and the monobutylamine (tertiary carbon) indicated the formation of compounds with hydrogen peroxide. These compounds are probably the first molecular complexes formed in the oxidation of amines to nitro compounds.

The oils which separate on mixing anhydrous ether solutions of amines and hydrogen peroxide were analyzed and shown to be molecular compounds of peroxide and the base.

An accurate determination of the heat of decomposition of hydrogen peroxide was carried out at 20° which gave the value 23,450 cal. for the molecular heat of decomposition into water and oxygen gas at atmospheric pressure.

A determination of the vapor density of hydrogen peroxide gave the molecular weight to be 34.

The decomposition of pure hydrogen peroxide was found to change rapidly in character about its boiling point, 151°, from that of a quiet reaction to a violent explosion. The addition of a little water or potassium chloride deadened the effect.

MONTREAL, CANADA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OR AGRICULTURE]

THE THERMAL DECOMPOSITION OF AMMONIA ON IRON CATALYSTS. II

BY C. H. KUNSMAN

RECEIVED AUGUST 24, 1928 PUBLISHED MARCH 6, 1929

The development of the following method of investigating catalysts and the results herein reported are the outgrowth of studies on the thermionic properties of the materials and mixtures used as catalysts in the synthesis of ammonia.[1] In order to determine the relative importance of the physical properties of the catalysts and to compare these properties with their catalytic properties, it was necessary to have some measure of the chemical activity of the surface at the same temperature and under as nearly the same surface conditions as when the thermionic measurements were made. The decomposition of ammonia was chosen rather than the synthesis as no appreciable or easily measured amount of ammonia is synthesized at one atmosphere pressure or lower and the present system and methods would not permit of working at higher pressures. The decomposition tests proved satisfactory in every way. The same developments which gave a very uniformly coated catalyst strip as a positive ion source, gave an equally uniform and constant temperature chemically active surface. The temperature of the surface was easily determined within a few degrees and kept constant at the given temperature throughout an entire test. The kinetics of the reaction of such a system are relatively simple in comparison to conditions in a catalyst bed as used in synthesis.

Since the publication of a preliminary account of this work[2] many more tests have been made on these catalyst mixtures, a detailed account of which will follow.

Apparatus.—The main scheme of the arrangement of the apparatus is similar to that used in the previous work[3] and is shown in Fig. 1. Instead of drawn filaments of tungsten, molybdenum or nickel, catalyst-coated platinum strips furnished the hot surface upon which the reaction took place. Very even and uniformly coated surfaces can easily be obtained when the catalyst mixture is first reduced, then finely ground and finally coated onto the strip. In this case the 300-mesh or finer catalyst, which has been ground under benzene, is mixed with paraffin and coated on to the hot strip by means of a glass rod at a temperature just high enough to melt the paraffin. When a thin but uniform layer is obtained on the twisted platinum strip, the temperature is raised by increasing the current through the strip. At a dull red temperature a bright red spot develops at some place on the strip and passes over the entire filament length.

---

[1] Kunsman, Phys. *Rev.*, **25,892 (1925)**; *Science,* **62,269 (1925)**; **J.** *Phys. Chem.,* **30, 525 (1926)**; *Phys. Rev.,* **27,249 (1926)**; *Proc. Nat. Acad., 12,* **659 (1926)**; **J.** *Franklin Inst., 203,* **635** *(1927).*

[2] Kunsman, *Science,* **65,527 (1927).**

[3] Kunsman, THIS JOURNAL, **50,2100 (1928).**

This bright spot is due to the heat produced by the rapid oxidation of the finely divided iron granules, and attains a temperature sufficiently high to sinter or fuse the coating to the twisted platinum strip. A coating of any desired thickness can be had by repeating the process as often as desired. This type of coating, even after reduction in hydrogen or nitrogen–hydrogen mixture, is very firmly attached and uniform in temperature. The only disadvantage is that the surface coated with the reduced material is relatively inactive in comparison to surfaces prepared by coating the platinum strip with the unreduced material. In the latter case the coating of the unreduced mixture and paraffin are applied to the filament and raised *to* a temperature just below visible and allowed to bake for about a half hour, after which another coating is applied and this continued until the desired thickness is obtained. This surface must be handled carefully as portions may break off and destroy the uniformity of the surface. The surface on reduction is very much more active catalytically than the previous one, as will be shown. As the ammonia catalyst is the reduced mixture and not the oxide, care was taken to see that the coated materials were thoroughly reduced either in a nitrogen–hydrogen mixture or hydrogen before the decomposition tests were made.

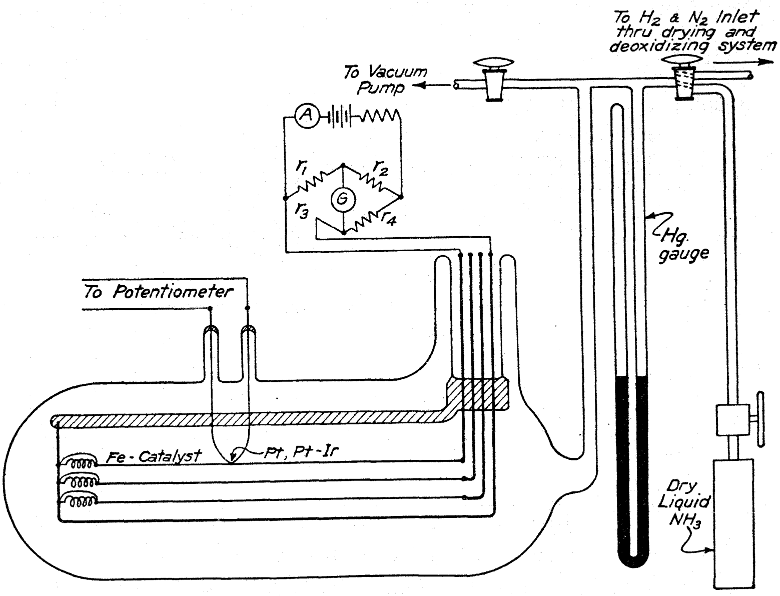


Fig. 1.—Apparatus for the study of the decomposition of ammonia on catalyst coated strips.

The temperature of the coated surface was determined in two ways: first, by means of an optical pyrometer, correcting for the emissivity of the surface and the absorption of the glass, and, second, by means of a thermocouple welded to the platinum strip. In this case the 0.005-cm. diameter Pt–Pt–Ir wire forming the juncture was close to the surface of the catalyst coating. The thermocouple is the more convenient method of determining the temperature and can be used through a wider range of temperatures than the optical pyrometer. Some difficulty was at first encountered in getting these fine wires through a pyrex glass. Any very slow leaks which may result at times at these seals can be closed with de Khotinsky wax.

The temperature as read from the calibrated thermocouple gave an added check on the Wheatstone bridge method of keeping the resistance of the filament and temperature of the hot surface constant throughout the run or until almost the whole of the ammonia was decomposed.

The coated strips were attached at one end through heavy tungsten leads and the other through *a* molybdenum spring and platinum strip. The function of the spring was to keep the filament taut and of the platinum strip to carry most of the current, so that no parts of the assembly would become appreciably hot except the coated surface. From four to eight amperes was used to heat the coated strip. The decomposition chamber w~ immersed in running tap water throughout all tests. A mercury trap, not shown in the sketch, separated the decomposition chamber and McLeod gage from the rest of the apparatus after the proper ammonia pressure, usually one-third of an atmosphere, was obtained.

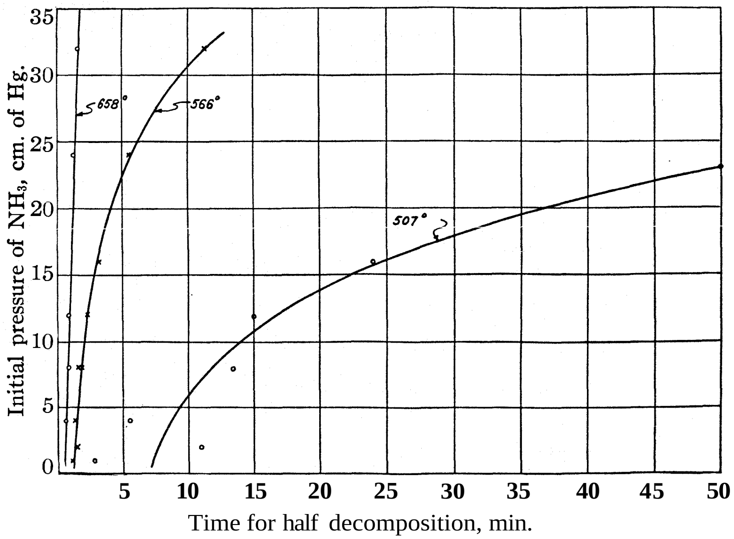


Fig. 2.—The decomposition of ammonia on a Fe–Al–K catalyst at 507, 566 and 658°.

Order of Reaction.—As the results from all the catalyst-coated strips were similar, a detailed account of one catalyst only will be given. In general the system is not as simple as the tungsten or molybdenum. The results obtained in an attempt to determine the order of the reaction are given in Fig. 2. One notices that there was no simple relation between the "half time" and the ammonia pressure, that is, the "half time" had neither a linear variation with the ammonia pressure (test for apparent zero order reaction) nor was it independent of the initial ammonia pressure (test for apparent first order reaction). One cause of this variation is quite evident when we consider the effects of the products of the reaction, nitrogen and hydrogen, on the reaction velocity. This effect can best be shown by referring to Fig. 3. Nitrogen has very little or no effect, while a very marked effect of hydrogen in slowing up of the reaction is apparent at 630°. The data of Fig. 3 were taken four months after those of Fig. 4. The two surfaces, therefore, are not comparable. In the previous results reported for tungsten and molybdenum a small but definite retarding effect was observed for hydrogen and but very little or no effect for nitrogen. In Fig. 2, at the highest temperature, 658°, where there is relatively little hydrogen adsorbed on the catalyst, there is little or no deviation from a straight line (zero order test), but at the lower temperatures, 566 and 507°, the deviation is very marked; since the effect of hydrogen in slowing up the reaction increases with a decrease in temperature, it may constitute the entire difficulty in determining the order of the reaction. Further tests are under way to clear up this point.

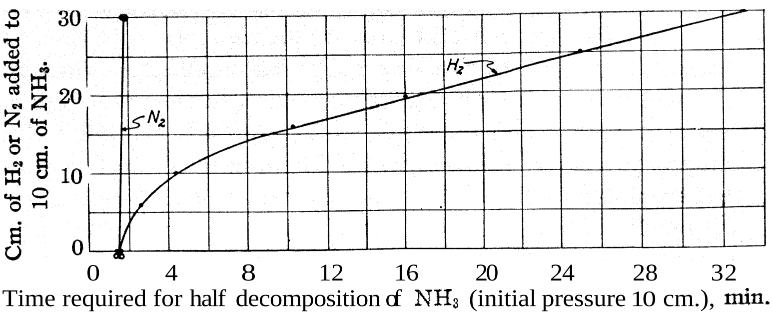


Fig. 3.—The effect of nitrogen and hydrogen on the rate of decomposition of ammonia on a catalyst surface at 630° (Fe–Al–K catalyst).

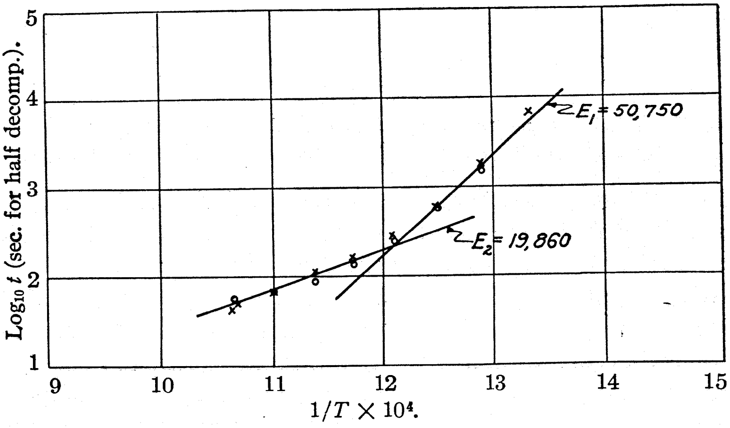


Fig. 4.—The temperature coefficient of the decomposition of ammonia on a catalyst surface (Fe–Al–K catalyst).

Determination of E.—The decomposition results will again be expressed in terms of Arrhenius' equation, rate of decomposition = $Ae^{-E/RT}$, where E will be determined from the temperature coefficient of the surface reaction as a function of the temperature. It is more obvious from Fig. 4 than in the previous work that a smooth curve drawn through all of the points will best represent the observed results, but again we will approximate the data by straight lines representing the range for values of E. Fig. 4 represents the data obtained from the surface when the activity of the surface had become constant after reduction. In this case an unreduced catalyst was coated and then reduced at a relatively low temperature. The test was taken by going from the high to the low temperature; the crosses represent these data, while circles represent the point obtained as the temperature was then increased, The failure of the two curves to be identical represents the effect of some change in surface. Fig. 5 (a) shows the results of a curve taken from one-fourth decomposition for the

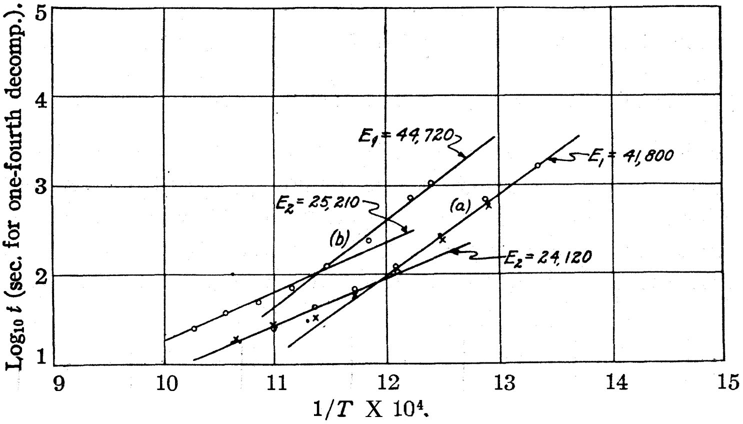


Fig. 5.—The temperature coefficient of **the** decomposition of ammonia on a catalyst, for (a) "1/4 time" and (b) "1/2 time" (Fe–Al–K catalyst).

same test as Fig. 4, in comparison to the other curve, Fig. 5 (b), taken after four months of experiments on the same filament. The values of E and general form of the curve are the same but a considerable shift to a higher temperature range or lower catalytic activity was observed.

The limit for the temperature range of the tests is determined by the length of the decomposition run. It was inconvenient to keep conditions constant over more than about five hours, time for half decomposition at the lowest rates, or to measure rates accurately at high temperatures where the time for half decomposition was less than a few minutes.

Promoters, Poisons and Heat Treatment Studies.—The results shown in Fig. 6 were taken considerably earlier and in a system somewhat different from that giving the other results. The four coated strips, about 10 cm. long and 1 mm. diameter, were mounted horizontally in a two-liter bulb. An effort was made to duplicate the method of coating, keeping the area of all the surfaces as nearly as possible the same. (a), (b) and (c) were mixtures that were first reduced and mixed with paraffin and flashed or coated at about 1000°. (a)[4] was a mixture containing the oxides of Fe–Al–Sn. (b) was a good grade of iron prepared in the form of a catalyst. (c) was one of the best catalysts developed for the synthesis of ammonia, being doubly promoted and containing Fe–Al–K. (d) was the same catalyst mixture as *(c)*, Fe–Al–K, but was powdered, mixed with paraffin and coated in the unreduced form at about 350°. This Fe–Al–K oxide mixture was first thoroughly reduced in an atmosphere of $N_2 + 3H_2$ mixture before being used. The results are in general agreement with their relative activity in the synthesis of ammonia,[5] but, due to the very different conditions as to pressure and method in the synthesis and decomposition, nothing more than a relative comparison can be made. Tin is a very bad poison for a catalyst in the synthesis of ammonia and shows up as having the lowest activity in the decomposition. In comparison to (b), which is a straight iron catalyst, we may say that the tin has the effect of decreasing the rate of decomposition. On the other hand, the Al–K oxide promoter gives a more active catalyst than (b). The relative activity of (d) to (c) is due, undoubtedly, largely to the freedom of sintering in (d) caused by the difference in the method of coating. In this case a 10-fold increase in activity is observed at 527° of (d) over (c).

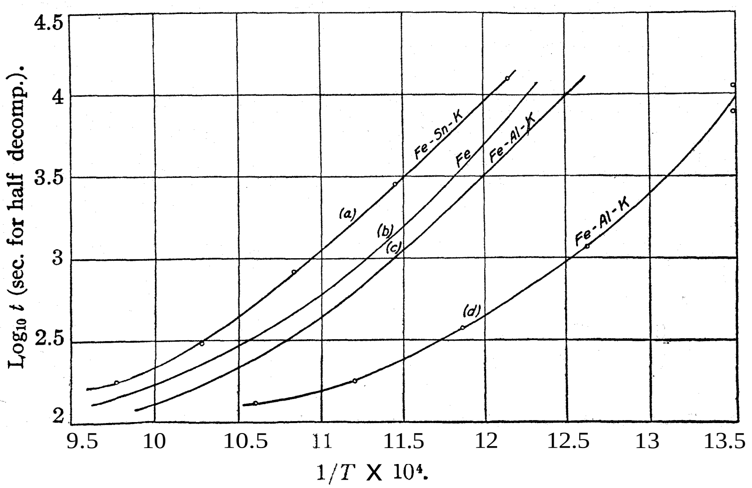


Fig. 6.—The effect of a promoter, poison and heat treatment on the rate of decomposition of ammonia on a catalyst surface.

All curves are of the same general nature, being displaced according to temperature alone. The effect of a promotor and low temperature coating

---

[4] Larson and Richardson, *Ind. Eng. Chem.*, 17,971 (1925).

[5] Almquist and Crittenden, *ibid.*, 18, 1307 (1926); Larson and Brooks, *ibid.*, 18, 1305 (1926).

is to displace the activity curve toward a lower temperature, while the effect of a poison is to displace the curve toward a higher temperature. These curves, including a difference of 16-fold activity at a given temperature, lead one to conclude that again the A or surface constant is of prime importance in determining the relative catalytic activity of these surfaces; that is, the effect of a promoter or poison is to increase or decrease, respectively, the amount of active surface or parts of the surface upon which the decomposition may take place, and is in accord with previous operations on these catalysts.[6]

Figure 7 gives for comparison the relative activity per sq. cm. for the various surfaces tested to date. The catalyst surfaces were determined from careful measurements of the diameter and length of the coated strips.

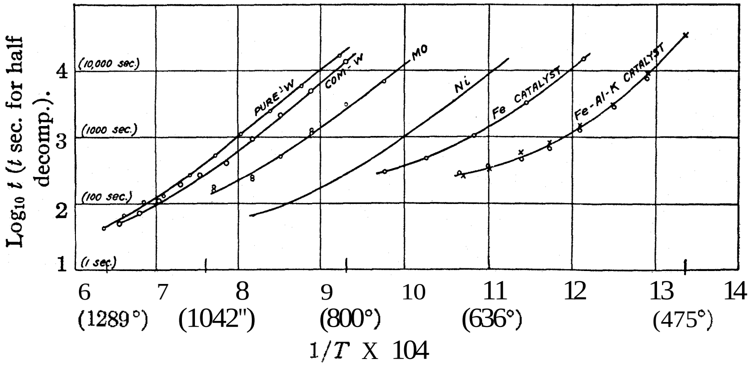


Fig. 7.—The relative activity of metal catalysts per square centimeter of surface for the decomposition of ammonia.

This method was used in the absence of a better method of comparison. These coated strips have more irregular surfaces than the drawn filaments previously tested. It appears from a careful inspection that all coated catalyst surfaces have about the same degree of roughness or irregularity and can therefore be dealt with as having about the same surface exposed to the ammonia gas. An effort was made to determine the activity of a drawn iron filament similar to nickel but without success. Due to bright spots resulting in an uneven temperature and the like, no complete run was obtained. From some individual tests we conclude that the iron curve would come close to the nickel curve.

We notice these marked similarities in all curves; first, that no single straight line will represent the data for an entire temperature range; second, that the more active the catalyst, the more marked deviation from a straight line, or the larger the variation in E with temperature. Drs. W. E. Deming and P. H. Emmett of this Laboratory have recently shown that

---

[6] Almquist, THIS JOURNAL, 48,2820 (1926).

with an increasing adsorption of the products accompanying a decrease in temperature, less surface will be available for decomposition and that the relation between E and T will be a curve similar to the observed graph, Fig. 6, and not a straight line relation. These results will be published later.

The author wishes to express his appreciation to Dr. F. G. Cottrell, Director of the Laboratory, for suggestions and encouragement in this work; to Dr. E. D. Crittenden for valuable assistance in the early stages of the work; to Dr. P. H. Emmett for criticisms of this paper; to Mr. E. S. Lamar for assistance in the experimental work, and especially to Mr. R. A. Nelson for construction of apparatus and assistance throughout these studies.

Summary

The decomposition of ammonia on catalyst surfaces coated on platinum has been investigated and the results have been expressed and interpreted in terms of Arrhenius' equation. The data show that both the A and the E constants vary with temperature for a given catalyst.

The order of the reaction is not a simple one, on account of the retarding effect of hydrogen. The effect of hydrogen varies with the temperature of the catalyst, being small at the higher temperatures but large at the lower temperatures. Nitrogen has no appreciable effect on the rate.

The value of E as determined from the temperature coefficient varies from about 50,000 at the lower temperatures to 20,000 at the higher temperatures.

The effect of a promoter, poison or heat treatment of the surface is to displace the activity curve toward a lower or higher temperature, respectively, without any appreciable change in the form of the curve.

A summary of all of the surfaces tested shows that not only is the metal or mixture important, but of equal or more importance is the method of preparation of the catalyst surface and the heat treatment of the surface.

The results obtained indicate that no simple or easily interpretable meaning can be given to A or E, whereby the exact role played by the catalyst can be determined.

Tests are now in progress, the results of which promise to permit of a rigorous kinetic treatment.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LOW TEMPERATURE RESEARCH STATION]

THE THERMODYNAMIC ACTIVITIES OF THE PROTEINS

BY G. S. ADAIR[1]

RECEIVED SEPTEMBER 4, 1928 PUBLISHED MARCH 6, 1929

I. Introduction

In solutions of finite concentrations the osmotic pressures of protein salts may be very different from the values predicted by the ideal solution laws.[2] This paper is concerned with the derivation of formulas correlating the thermodynamic activities of protein salts with the measurements of osmotic pressure and the practical application of these formulas to a salt of hemoglobin.

The empirical formula for a salt like the sodium hemoglobinate, $HbNa_n$, includes a number, n, which is not an integer, because it represents the average number of sodium atoms combined with a protein molecule, in a system in which the number of atoms combined with individual protein molecules may have a wide range of variation. The average value of n is a variable ranging from 0 to 80 in accordance with variations in the activities of sodium and hydroxyl ions.

In certain respects there is a close resemblance between protein salts and typical strong electrolytes, but the theoretical and experimental treatment of the activities of protein salts is modified by the condition that n is neither an integer nor a constant independent of the concentrations of diffusible electrolytes.

II. Thermodynamical Relationship between the Osmotic Pressures and the Average Values of the Potentials and Activities of Protein Salts

The activity or effective concentration of a protein salt is here defined by Formula 1.

$$\mu_{ps} = RT \ln a_{ps} + K_1 \tag{1}$$

K_1 = a constant, defined by the convention that the activity equals the concentration in very dilute solutions. μ_{ps} = the "average value" of potential of the protein salt per gram mole, at the temperature T and the pressure P. a_{ps} = the "activity" of the protein salt, defined by this formula, and is the antilogarithm of the "average value" of $\ln a_{ps}$ in the assemblage of salts represented by an empirical formula of the type $HbNa_n$.

It is well known that the potential or activity of a single substance can be determined by the application of Gibbs' equations[3] (Lewis and Randall[4])

---

[1] Fellow of King's College, Cambridge.

[2] G. S. Adair, *Proc. Roy. Soc. London*, 120A, 573 (1928).

[3] J. W. Gibbs, *Trans. Conn. Acad.*, 3, 108 (1876); "Scientific Papers," New York, 1906, p. 88.

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

and under certain conditions, discussed below, it is possible to determine the average value of the potential, μ_{ps}, by the application of Equation 2, a restatement of Gibbs' equation numbered 97.

$$VdP = \eta dT + m_{ps}d\mu_{ps} + m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n \qquad (2)$$

V = the volume of the solution; P = the hydrostatic pressure. η = the entropy of the system; T = the absolute temperature; m_{ps} = mass of the protein salt in gram moles in the volume V; m_1 = the mass of water in gram moles; m_2, m_n, denote the masses of other crystalloids; μ_1 = the potential of water; and μ_2, μ_n = the potentials of other crystalloids.

The conditions that the protein system must be stable and that the protein itself must be equivalent to one component can be realized in solutions of hemoglobin at 0°.[2] The protein system, however, differs from an aqueous solution of a typical strong electrolyte in that the presence of a third component such as sodium hydroxide is a condition for the existence of a salt like sodium hemoglobinate. In this work the number of diffusible components has been increased to four by the addition of phosphate mixtures, in order to maintain the protein salt at well-defined hydrogen-ion concentrations.

The practical application of Gibbs' formula is simplified if some of the variables are kept constant, so that their differentials can be omitted, as stated in Formulas 3 and 4 below.

$$m_{ps}d\mu_{ps} = -m_1 d\mu_1 - m_2 d\mu_2 \ldots\ldots - m_n d\mu_n \qquad (3)$$

μ_{ps} symbolizes the potential of the protein in systems where T, P and m_1, m_2, m_n are constants and m_{ps} is varied.

In the protein systems considered in this work the degree of accuracy obtained in measurements of osmotic pressure is much greater than the accuracy attainable in the measurements of the potentials of the diffusible substances, and therefore the calculations of μ_{ps} have been made by Formula 5 (derived from Formula 4 below) rather than the well-known and theoretically more accurate Formula **3.**

The function $(\mu_{ps})_\mu$ defined by Formula 4 differs from μ_{ps} because it refers to conditions where T, μ_1, μ_2, μ_n are constant and the hydrostatic pressure **P** is a variable.

$$m_{ps}d(\mu_{ps})_\mu = VdP = Vdp \qquad (4)$$

In the experiments described below the potentials of the crystalloids have been kept constant by the equilibration of the protein solutions in collodion membranes with a standard solution of crystalloids in which the temperature, the hydrostatic pressure P'' and the composition have been kept constant. Gibbs' equation for membrane equilibrium (No. 77) shows that μ_1, μ_2, μ_n are then constant in the protein solutions, as they are constant in the standard solution or "outer fluid."

p = the observed osmotic pressure is here defined as the pressure difference $P - P''$, measured with a membrane permeable by all the crystalloids but impermeable by protein, under conditions where the protein concentration is varied, T and μ_1, μ_2, μ_n are constants and P'' is equal to 1 atmosphere.[5]

Since the function $(\mu_{ps})_\mu$ refers to a special set of conditions, the results calculated by Formula 4 require correction before they can be compared with the observations on solutions of crystalloids published by previous workers.

In general this correction is complicated by the fact that the "solvent" is not a pure substance but a mixture with three or more components. In the protein systems considered below m_{ps} is relatively small and it appears that a correction which is accurate enough for the purpose of this work can be obtained by assuming that $d(\mu_{ps})_\mu$ is equal to $(\partial\mu_{ps}/\partial P)dp + d\mu_{ps}$.

It is known that the effect of hydrostatic pressure on the potential of a component is represented by an equation of the form $(\partial\mu_{ps}/\partial P) = \bar{v}_{ps}$, where $\bar{v}_{ps}$ is the partial specific volume of the protein salt per gram mole, and it follows that μ_{ps} at a constant hydrostatic pressure is determined by Formula 5.

$$m_{ps}d\mu_{ps} = Vdp - m_{ps}\bar{v}_{ps}dp \tag{5}$$

The determination of the conditions under which the simple Formula 5 is equivalent to Formula 3 is facilitated by the consideration of the "corrected osmotic pressure $(P - P'')$ P where the protein solution is at a constant pressure, P, and the "outer fluid" is at a pressure P'' less than one atmosphere.

It will be assumed that under these conditions the protein solution can be composed of two mixtures, each of which is of constant composition. The composition of the first mixture, designated the "solvent," is the same as the composition of the fluid outside the membrane. The second mixture, designated the "protein salt," includes the pure protein and a certain proportion of the crystalloids that are present in excess inside the membrane.

If these two mixtures of constant composition are treated as the components of the system, a formula for μ_{ps} in terms of μ_x', the potential of the "solvent," can be obtained by the application of Equation 3 as stated in Formula 6. The theory of membrane equilibrium shows that $\mu_x' = \mu_x''$, the potential of the "solvent" in the outer fluid, and by Formula 2 $\mu_x'' = v_x''dP''$, where v_x'' is equal to the volume of one mole of the mixture in the outer fluid at the pressure P''. The corrected osmotic pressure can then be correlated with $d\mu_x'$ and $d\mu_{ps}$ by Formula 6.

$$m_{ps}d\mu_{ps} = - m_x'd\mu_x' = + m_x'[v_x''d(P - P'')_P] \tag{6}$$

---

[5] p is very much smaller than the osmotic pressure measured by a membrane permeable by water only (sympolized π in Formula 11). The relationship between π and the activity of a colloid in an aqueous solution has been worked out by Linderström-Lang, *Compt. rend. Lab. Carlsberg*, **16** (1926).

m'_x = gram moles of "solvent" in the solution containing m_{ps} gram moles of protein.

Experimental evidence given below indicates that the observed and the corrected osmotic pressures are in close agreement, and it follows that Formulas 5 and 6 are equivalent to the simplified Formula 7.

$$v_s dp = (V' - \bar{v}_{ps})dp = d\mu_{ps} = RT\,d \ln a, \tag{7}$$

v_s = liters of solvent per mole of protein. $V' = V/m_{ps}$ = liters of solution per mole of protein.

A formula for the potentials and activities of protein ions (No. 8) can be obtained by the application of Formula **2** to a system in which the individual ions are treated as components. In the case of the sodium proteinate, $HbNa_n$, it is simpler to replace d ln *a*„ in Formula *7* by the equivalent expression d ln *a*, + n d ln a_{Na}, derived from Formula **12.** Since $n = -n_p$, where n_p is the average valence of the protein ions, Formula **13** shows that $n \, d \ln a_{Na} = (n_p F/RT)dE$, where E = the membrane potential.

In the derivation of Formula 8 below, a small correction for the effects of pressure on the activities of the diffusible ions has been omitted

$$v_s dp = d\mu_{ps} = d\mu_p + n_p F dE = RT\,d \ln a, + n_p F dE \tag{8}$$

μ_p = average value of the potential of the protein ions; *a*, = (logarithmic) mean value of the activity of the protein ions; *n*, = mean valence of protein ions, defined as the equivalent cencentration divided by the molar concentration.

III. Definitions of the Standard State of a Protein Salt and the Functions *a*„ and *a*,

Relative values of the potentials and activities can be calculated by integrating Equations 7 and 8, as stated in Formulas **9** and **10,** on the assumption that the composition of the protein salt is constant over the range of osmotic pressure from p° to p'. Experimental evidence concerning the degree of accuracy of this assumption is referred to below.

$$\int_{p^\circ}^{p'} v_s dp = \mu'_{ps} - \mu^\circ_{ps} = RT \ln a'_{ps} - RT \ln a^\circ_{ps} \tag{9}$$

$$\int_{p^\circ}^{p'} v_s dp = \mu'_p - n_p FE' - \mu^\circ_p - n_p FE^\circ \tag{10}$$

There are two conventional definitions of the "standard state" of the protein salt that must be considered in fixing the absolute values of the activities by Formulas **9** and **10.**

The "Hypothetical Standard State" is a very dilute solution of the protein salt in the absence of diffusible crystalloids. The theoretical osmotic pressure of such a salt is given by Formula 11.

$$\pi = (1 + n)C_p RT \tag{11}$$

C_p is the molar concentration and n the number of sodium atoms in the salt $HbNa_n$. With this definition of the standard state, the activity of the protein salt is comparable with the activity of typical strong electrolytes and the following formula may be applied.

$$(a_{ps})_w = (a_p)_w \, a^n_{Na} \qquad (12)$$

(a,,), and *(a,),* denote the activities of the protein salt and the protein ion referred to the hypothetical standard state. These activities cannot be determined by direct methods because the protein salt cannot exist in the theoretical standard state. Indirect methods of estimating these activities and a function f_0 referred to below will be discussed in a later paper. a_{Na}, the activity of sodium ions, can be calculated from measurements of the membrane potential by Formula[6] **13** below, as described in a previous paper.[2]

$$\ln a'_i = \ln a''_i - n_i FE/RT \qquad (13)$$

a'_i = the activity of any diffusible ion (of valence n_i) in the protein solution. a''_i = the activity of this ion in the solution of crystalloids in diffusion equilibrium with the protein solution.

In this case a''_i = a constant and it follows that $d \ln a_{Na} = -(n_i F/RT)dE$.

The "Experimental Standard State" is a very dilute solution of the protein in diiusion equilibrium with the standard solution of crystalloids. The osmotic pressure, p, approaches the value C_pRT rather than $(1 + n)C_pRT$ under these conditions, as shown by the observations in Table I. The symbols a„ and *a,* denote activities calculated on assumption that a„ is equal to the protein concentration in the experimental standard state. The application of Formula 10 shows that a„ and a, are related by Formula 14

$$a_{ps} = a_p e^{n_p u} \qquad (14)$$

$u = EF/RT$, where E is the membrane potential; e = *2.718; a,* = the logarithmic mean value of the activity of the protein ions referred to the experimental standard state. In calculations of *a,* at 0°, from the data given below, Formula 14 can be replaced by 14a.

$$\log a„ = \log a, + n_pFE/2.303RT = \log a, + n_pE/0.0542 \qquad (14a)$$

The relationships between *a,* and a„ and the activities referred to the hypothetical standard state are given below. *(1)* d ln *a,* is equal to d In *(a,)„* and therefore *(a,),* is equal to f_0 a„ here f_0 is an undetermined integration constant. (2) The application of Formula **13** shows that $a_{Na} = a''_{Na}e^{-u}$, and it follows that *(a,,),* $= f_0(a''_{Na})^n a_{ps}$.

The experimental investigations recorded below refer to the functions a„ and a,. The determination of f_0 and *(a,,),* with the assistance of solubility measurements may be considered, but the thermodynamic treatment of solubility measurements must be postponed, because the

---

[6] F. G. Donnan and J. H. Allmand, J. Chem. *Soc.,* **105, 1941 (1914).**

composition of the crystalline phase is not a constant but a function of the concentrations of diffusible electrolytes.[7]

IV. Experimental Investigations

Five groups of measurements are required for the application of the thermodynamic formulas for the activities of protein salts and protein ions.

1. A series of measurements of osmotic pressures and volumes under conditions where the potentials of the crystalloids are nearly constant, supplemented by measurements of the temperature, the pressure and the composition of the solution of crystalloids in diffusion equilibrium with the protein solution.

2. A series of measurements of the effects of the temperature, pressure and the concentrations of the crystalloids on the osmotic pressure at a constant protein concentration. These observations are required to reduce the observed pressures under slightly different conditions to those corresponding to the theoretical standard state in which the potentials of the crystalloids are absolutely constant.

3. Measurements of the magnitude of the error introduced by the assumption that the average composition of the protein salt is independent of the protein concentration under conditions where the potentials of the crystalloids are constant. In the system considered in this work the error due to this assumption appears to be relatively small.

4. Measurements of the partial specific volumes of "solvent" and solute are required in calculations of activities at a constant hydrostatic pressure.

5. Measurements of membrane potentials and the valences of protein ions are required in calculations of the activity of the protein ion.

The subsidiary investigations 2–5 are not quite complete and the numerical values of the activities given in this paper are provisional.

1. Measurements of Osmotic Pressure.—A critical study of the direct method of measuring the osmotic pressure of hemoglobin with collodion membranes permeable by water and salts but impermeable by the protein has been given in a previous paper.[8]

This method has been applied for the purpose of determining the relationship between osmotic pressure and protein concentration under conditions where the potentials of the crystalloids are practically constant.

Collodion sacs containing about 15 cc. of hemoglobin solution have been equilibrated with relatively large volumes of the "Standard Solution" of phosphates, specified in Table I. The results of 32 measurements of the osmotic pressure of hemoglobin in equilibrium with this standard solution have been published in the tables and curves given in a previous

---

[7] S. P. L. Sörensen, *Compt. rend. Lab. Carlsberg*, 12, *188* (1917). The solubility of hemoglobin in different mixtures of electrolytes has been measured by E. J. Cohn and A. M. Prentiss, J. *Gen. Physiol.*, *8,* 619 (1927).

[8] G. S. Adair, *Proc. Roy. Soc. London,* **108A,** 627 (1925).

paper.[2] Calculations of the "osmotic coefficients" for six of these observations are recorded in Table I. In dilute solutions the observed osmotic pressures approach the theoretical values given by van't Hoff's law stated in the form

$$p = C_pRT \tag{15}$$

$C_p = C_{Pr}$, in grams of dry protein, divided by 68,000, where 68,000 ± 2,000 is the molecular weight of sheep's hemoglobin expressed in grams of protein dried at 103°.[9]

TABLE I

OSMOTIC PRESSURES OF A SALT OF HEMOGLOBIN DESIGNATED[a] $Hb(Na + K)_{8.5}$

Conditions: the potentials of the crystalloids have been kept constant by the equilibration of the protein solutions with a standard phosphate mixture containing 0.1 mole of KCl, 0.0613 mole of Na_2HPO_4 and 0.00533 mole of KH_2PO_4 per liter of solution. The temperature of the standard solution is 0° and the hydrostatic pressure is 760 mm. p = observed osmotic pressure in mm. of mercury at 0°. $RT = 22.41 \times 760 = 17{,}033$ at 0°.

Hb per liter of soln., g. C_{Pr}	Hb per liter of soln., mole C_p	Osmotic press., obs., p	Osmotic press., theoretical RTC_p	Osmotic coeff., p/RTC_p
22	0.00032	6.15	5.5	1.11
80	.00118	28.2	20.0	1.42
200	.00294	110.9	50.1	2.21
240	.00353	155.0	60.1	2.58
290	.00426	264.6	72.6	3.64
344	.00506	382.8	86.1	4.44

[a] The formula $Hb(Na + K)_{8.5}$ is provisional. A discussion of the complete formula for the protein salt as it exists in the solution will be given at a later date. The number of Na + K atoms combined with hemoglobin in blood is approximately the same as the number in the salt considered in this paper.

2. Corrections for Deviations from the Standard State.—The actual conditions in different experiments recorded in Table I did not correspond exactly with the theoretical standard state, namely, a solution of reduced hemoglobin in equilibrium with a solution containing 0.1 mole of KCl, 0.0613 mole of Na_2HPO_4 and 0.00533 mole of KH_2PO_4 at 0° and 760 mm.

The effects of different variables at a protein concentration (about 190 g. per liter) which gives a pressure of 100 mm. in the standard state have been summarized below.

(i) An increase in temperature from 0 to 1.0° raises the osmotic pressure from 100 mm. to 100.36 mm.

(ii) An increase in the barometric pressure from 760 to 775 increases the osmotic pressure from 100.0 to about 100.02 mm.

(iii) An increase of 10% in the total concentration of crystalloids diminishes the osmotic pressure from 100.0 mm. to 99.6 mm.

(iv) An increase in the hydrogen-ion concentration due to carbon dioxide which

---

[9] G. S. Adair, *Proc. Camb. Phil. Soc. Biol.*, *1*, 75 (1924); *Proc. Roy. Soc. London*, **109A**, 292 (1925); T. Svedberg and R. Fåhraeus, THIS JOURNAL, 48, 430 (1926); T. Svedberg and J. B. Nichols, *ibid.*, 49, 2920 (1927).

corresponds with a change in PH from 7.80 to 7.60 diminishes the pressure from 100.0 mm. to 99 mm.

(v) The oxygenation of the hemoglobin and the formation of met-hemoglobin cause relatively little change in the observed osmotic pressure.

The variations considered above are greater than any that have been observed in the experiments included in Table I.[2] It seems probable that the observed pressures are within about 2% of the corrected pressures for the theoretical standard state.

3. The Effects of Variations in **the** Average Composition of the Protein Salts.—In practice it is impossible to alter the total concentration of a protein without altering some of the conditions which determine the proportions of individual protein salts and the average compositions of the mixture.

If the concentration of a protein salt is increased at a constant hydrogen-ion concentration, there is an alteration in the interionic attractions which tends to increase n, the average number of atoms of sodium in a salt like sodium hemoglobinate.[10]

If the concentration of the sodium hemoglobinate is increased under conditions where the potentials of the crystalloids are constant, there is an increase in a_{H}, the activity of hydrogen ions, (Table II) or a diminution in PH (= $-\log a_{\mathrm{H}}$) which tends to diminish the value of n by approximately 10 units for a diminution of 1 unit in the PH. This estimate is based on the observations of Van Slyke and other workers, referred to in a previous paper.?

The range of variation in PH from 7.80 to 7.77 (shown in Table II) diminishes n from about 8.5 to 8.2, and it seems unlikely that this change is exactly balanced by the effects of interionic forces.

It has been stated that Formulas 9 and 10 are not valid if n is not a constant, and therefore it is necessary to consider the error due to a variation in n. In the previous section it has been pointed out that a variation in the hydrogen-ion concentration from PH 7.8–7.6 alters the osmotic pressure p by about 1%, and therefore it appears that the variation in n caused by a much smaller change in hydrogen-ion concentration cannot have any great effect on the pressure p or the function a,,, which is defined in terms of osmotic pressures. The absolute value of n does not enter into the formula for a,,. In the case of the function (a,,),, which is equal to $(a_{\mathrm{p}})_w a_{\mathrm{Na}}^n$, the absolute value of n and the effects of slight variations in n are of much greater significance.

4. The Partial Specific Volumes of the Solvent and the Protein.—v_x'' = the volume of 1 mole of the standard solution (Table I). $\bar{v}_x$ = the "partial specific volume" of 1 mole of this mixture in the protein solution. $\bar{v}_{\mathrm{ps}}$ = the partial specific volume of 1 mole of the hemoglobin.

Preliminary investigations show that the ratio $\bar{v}_x/v_x''$ varies from 0.9998

---

[10] S. P. L. Sörensen, K. Linderström-Lang and E. Lund, J. *Gen. Physiol.*, **8**, 543 (1927).

at low protein concentrations to 0.999 at higher concentrations. The application of the formula[11] $(\partial p/\partial P) = (1 - \bar{v}_x/\bar{v}''_x)$ shows that the observed osmotic pressure, p, is not appreciably different from the theoretical pressure $(P - P'')_P$ in Formula 6.

The measurement of $\bar{v}_{ps}$ is more difficult because the protein cannot be dried without irreversible changes. As a first approximation it appears that $\bar{v}_{ps}$ is about 65 liters.[2]

5. The Membrane Potentials of the Protein Solutions.—A table of measurements of membrane potentials with saturated calomel electrodes has been given in a previous paper.[2] Calculations based on six of these observations recorded in Table II show that the simple empirical formula No. 16, agrees with the observed results within the limits of experimental error

$$E = -0.24\, m_p \tag{16}$$

m_p = moles of protein per liter of solvent $= C_p/(1 - 65\, C_p)$.

TABLE II

MEMBRANE POTENTIALS AT DIFFERENT HEMOGLOBIN CONCENTRATIONS

Conditions: hemoglobin solutions in equilibrium with Standard Solution in Table I. $KCl + Na_2HPO_4 + KH_2PO_4$ at 0° ($P_H = 7.8$).

Hb per liter of soln., moles, C_p	Hb per liter of "solvent," moles, m_p	Membrane potential, (obs.), mv.	Membrane potential (calcd.), mv.	Corr. P_H of soln.
0.00032	0.00033	−0.07	−0.08	7.799
.00147	.0016	− .50	− .38	7.791
.00294	.0035	− .87	− .87	7.784
.00353	.0046	−1.05	−1.10	7.781
.00426	.0059	−1.45	−1.42	7.773
.00506	.0075	−1.98	−1.80	7.764

6. The Mean Valence of Protein Ions.—The mean valence of the protein ions is equal to the "equivalent concentration" of the protein divided by its molar concentration. This equivalent concentration must be equal to the difference between the equivalent concentrations of diffusible anions and cations that exist in the free state, uncombined with protein.

The concentrations of the free ions in the solution of strong electrolytes outside the membrane can be determined (Table I) and a provisional estimate of their concentrations in the protein solution can be obtained by applying Donnan's formula (13) to the membrane potentials recorded in Table II. It appears that $n_p = -5.9/f_e$, where f_e is a constant which is equal to unity if the concentrations of the ions are equal to their activities. If $f_e = 0.7$, then $n_p = -8.5$. The figure −8.5 has been adopted in the provisional calculations recorded in Table III. A revision of these calculations will be published when n_p has been determined by more accurate methods.

---

[11] A. W. Porter, *Proc. Roy. Soc. London*, **79A,** 519 (1907).

V. The Activity Coefficients of a Salt of Hemoglobin and its Ions

The activities of protein salts referred to the experimental standard state are different from the activities referred to a hypothetical solution of the protein salt in water, and therefore Formulas 17 and 18, which define the coefficients f_{ps} and f_p, are different from the conventional definitions of the activity coefficients of strong electrolytes.

$$RT \ln f_{ps}m_p = RT \ln a,. = \int v_s \mathrm{d}p + \text{constant} \quad (17)$$

m_p = gram moles of protein salt per liter of solvent and $f_{ps} = a_{ps}/m_p$ is a coefficient which approached unity at low protein concentrations, as shown in Table III. The integration constant is determined by this condition and by the condition that p approaches RTm_p when m_p is very small.

The chief diierence between f_{ps} and the activity of a typical strong electrolyte is due to the application of this formula rather than Formula No. 11, $a = (1 + n)C_pRT$. The function f_{ps} is not useful in comparisons of the properties of protein salts and crystalloids, but it is of importance as a step in the calculations off,, the activity coefficient of the protein ion, and in the treatment of the equilibrium of protein salts in gravitational fields of force, a subject which will be discussed in a subsequent communication.

The activity coefficient f_p defined by the formula $f_p = a_p/m_p$ can be calculated by Formula 14a, or Formula 18 given below.

$$m_pf_{ps} = m_pf_pe^{n_pw} \quad (18)$$

Since $(a,)$, is equal to f_0a_p, where f_0 is an indetermined constant, the product f_0f_p is comparable with the activity coefficient of an ion defined by the formulas of Lewis and Randall, although the resemblance is not quite exact, because f_0f_p is an "average value" and n_p is an average valence.

The results recorded in Table III show that the function f_p increases as the protein concentration increases. An increase in the partial osmotic pressure of the protein ions under these conditions has been referred to in a previous paper.'

A discussion of the kinetic significance of the rise in the activity coefficient is not permissible in a purely thermodynamical treatment of osmotic pressures and activities but there are one or two points which are of interest in connection with the application of the interionic attraction theory of Debye and Hückel to protein ions.

The absolute values of f_p increase as the protein concentration increases, a variation in the opposite direction to that predicted by the theory. **If,** however, the increase in f_p is compared with the increase in f_{pi}, the activity coefficient **of** the isoelectric protein, it appears that the "relative activity coefficient" (f_p/f_{pi})[12] diminishes from 1.0 to 0.8 as the protein concentra-

---

[12] **The ratio (f_p/f_{pi}) has been referred to in a preliminary note on the activity of protein ions,** Adair, *Trans. Faraday Soc.*, *23,* **536** (1927).

tion increases from 0.0 to 0.004, and in this respect the protein salt resembles a typical strong electrolyte.

TABLE III

THE ACTIVITY COEFFICIENTS OF A SALT OF HEMOGLOBIN AND ITS IONS

Conditions: temperature, 0°; pressure, 760 mm.; composition of "solvent," 0.10 mole of KCl, 0.0613 mole of Na_2HPO_4, 0.00533 mole of KH_2PO_4 per liter. Composition of protein salt, Hb $(Na + K)_{8.5}$. Valence of protein ion, $n_p = -8.5$. The membrane potential factor (Formula 14) is calculated from data given in Table II. The activity coefficients of the sodium and potassium ions are approximately equal to 0.7.

Hb per liter of solvent, mole, m_p	Act. of protein salt,[a] a_{ps}	Membrane potential factor, $e^{n_p w}$	Act. coeff. of salt, f_{ps}	Act. coeff. of ion, f_p
0.0002	0.0002	1.02	1.05	1.03
.0010	.0014	1.09	1.40	1.3
.0020	.0040	1.20	2.0	1.7
.0030	.0090	1.30	3.0	2.3
.0040	,0200	1.40	5.0	3.6

[a] The determination of a,, by the evaluation of the integral in Formula 17 may be facilitated by application of the empirical formulas discussed in a previous paper.[2] In dilute solutions the formula $p(v_s - b) = RT$ can be applied and by integration RT ln a,, $= \int v_s dp = RT$ In $p + bp$. Over the range of pressures from 12 to 120 mm., a formula with two empirical constants can be applied, $p(v_s - 107.5) = 1.09$ RT.

Conclusions

Under certain conditions the salt of a protein such as a sodium hemoglobinate is equivalent to one component, although the variations in the average composition of the salt caused by alterations in the activities of diffusible acids and bases prove that the sodium hemoglobinate is a mixture of a great number of individual protein salts.

The conditions for the application of Gibbs' equations to determine the "average values" of the potentials and activities of protein salts have been considered and the following formula has been obtained.

$$RT \text{ In } a, = RT \text{ In } a_p e^{n_p w} = \int_{p^\circ}^{p} v_s dp + \text{constant}$$

ln a,, and ln a_p denote the logarithmic mean values of the activities of the protein salt and protein ion; n_p = the average valence of the protein ion; u $= EF/RT$, where E = the membrane potential; v_s = the volume of "solvent"—(a mixture) per gram mole of protein; p = the osmotic pressure measured with a collodion membrane under conditions where the potentials of the diffusible salts are kept constant by the equilibration of the protein with a standard solution of crystalloids at a constant pressure and temperature.

The integration constant is determined by the convention that a,, is equal to the protein concentration in a very dilute solution in equilibrium with the standard solution of crystalloids. The relationship between a,, and the activities of typical strong electrolytes has been formulated.

The activity of a salt of hemoglobin has been investigated by experiment in order to determine the degree of accuracy in the assumptions that have been made in the thermodynamical treatment of a salt of variable composition in a system of many components.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

SPECIFIC HEATS OF SODIUM AND POTASSIUM HYDROXIDE SOLUTIONS[1]

BY THEODORE W. RICHARDS AND LAWRENCE P. HALL

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

In a previous publication[2] from this Laboratory it was pointed out that a serious discrepancy existed between the value then found for the specific heat of $NaOH\cdot 25H_2O$ and earlier values. Since this datum was to be made the basis for the specific heats of other solutions, heats of dilution, heats of neutralization, etc., the new and higher value demanded confirmation.[3] Hence part of the work was repeated with even greater care, especially studying possible sources of error and inaugurating a few slight modifications and improvements in procedure. The outcome was in general essentially in accord with the work of Richards and Gucker, as will be shown.[4]

Procedure with Modifications

The twin calorimeter system used previously was rebuilt in essentially the same form as described on pp. 1878–1881 of ref. 2. Standardization of new thermocouples showed a sensitivity of 0.000340" per mm. of scale reading for the larger thermocouple and 0.000527° per mm. for the smaller ones. Slight changes in the apparatus made it necessary to redetermine the water equivalent. Later it was found advisable to use a smaller amount of liquid in each can to avoid errors from splashing or spilling in assembling and handling the apparatus.

The chief causes of minor variations were found in maintenance of adiabatic conditions at all times and in trouble from unequal evaporation from the calorimeter cans, one containing water and the other solutions. The former difficulty was in part eliminated by trying out and adjusting

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript prepared by the junior author.

[2] Richards and Gucker, THIS JOURNAL, 47,1876 (1925).

[3] Earlier records present a bewildering variety of specific heat values for sodium hydroxide solutions, particularly for the more concentrated ones. Richards and Rowe, [THIS JOURNAL, 43, 770 (1921)] took 0.855 for $NaOH\cdot 10H_2O$—choosing from among old values ranging all the way from 0.84 to 0.89. It will be shown that this choice, although perhaps the best possible at the time, was much too low in value.

[4] **Ref.** *2* and the following paper in this series.

the heaters before the experiment, and for this purpose the solutions were put in at a temperature below that at which the experiment proper was to begin. The calorimetric system was then warmed to nearly 16° and during this period of heating the controls were so adjusted that conditions could be kept continuously adiabatic during the measured rise in temperature from 16 to 20". The fore and after drifts were measured as before.

Some variation in adiabatic conditions arose because the small thermels in the outer bath were sensitive to the radiations from the heating lamps. The use of the two 40-watt lamps was discontinued. Also, the thermocouples were placed so that they were shielded from direct radiation of the carbon lamps.

The errors from evaporation have been discussed[5] and likewise methods for their prevention and control. Paper collars were again used. However, from careful observation it appeared that closed calorimeter cans, with the minimum of air space above the solution and water, would be necessary to prevent this source of error.[6]

With conditions exactly adiabatic, unequal evaporation occurred in the two calorimeter cans, due in part to an adsorption effect on the inner surface of the submarine covers. Also it was found on exploration with sensitive thermometers that the surface of the outer bath, on account of evaporation into the room, could become slightly cooler than the bulk of the bath, thereby cooling the submarine lids and encouraging condensation. Since it was not practicable to cover this bath, as has often been done in this Laboratory, the amount of water was increased and the stirrer adjusted so that it drew water more rapidly from below.

Evaporation difficulties were further diminished by keeping the temperature of the outer bath slightly higher than formerly. At 16° with a thermal head of $+0.005$ to $+0.007°$ very little change in the temperature of the calorimetric system itself occurred in the fore period, during which the drift was found to be smaller and more regular. Similar benefits resulted from gradually increasing the thermal head during the course of the heating to a final value of $+0.007°$. Such a positive head would not appreciably influence the temperature of either calorimeter. It was found that when the temperature of either or both of the calorimeters was above that of the bath, peculiar and erratic drifts were obtained. For this reason another slight change in procedure was made when it so happened that a difference in temperature between the water and solution resulted during the heating period. Instead of holding the outside bath at the average temperature of the two cans, it was kept at least as warm as the warmer can. In this way the drifts were made more uniform without introducing any serious error from thermal leakage.

---

[5] Ref. 2, p. 1882.

[6] Cf. Gucker, THIS JOURNAL, 50, 1005 (1928).

Purification of Sodium Hydroxide

Except for these minor modifications, the experiments were performed in much the same way as described by Richards and Gucker.[2] The sodium hydroxide solutions were prepared as before, except that after crystallization of the hydroxide in platinum and separation of the insoluble sodium carbonate, a small amount of barium hydroxide solution, freshly prepared from recrystallized material, was carefully added to remove the last trace of carbonate. Any excess of barium was not desired. However, on some occasions when a slight trace was found, it was removed with a trace of sulfuric acid.[7]

The solutions thus prepared were apparently free from sulfate, barium, carbonate and chloride. It was later found that a slight amount of potassium was present, amounting (in the case of the solution used in the present work for the specific heat of $NaOH \cdot 25H_2O$) to between 0.1 and 0.2% of potassium (compared with the sodium present). This result was attained by difference through analysis as sulfate and hydroxide, and by direct comparison with similar amounts of precipitate produced with sodium cobalti-nitrite with known standards of similar composition.

In commercially "pure" samples of sodium hydroxide similar to that used for crystallization, sometimes as much as 0.3% of potassium was found; this impurity was reduced to about 0.1% by one crystallization. After a second recrystallization (as in the case of the solution $NaOH \cdot 101H_2O$) no test for potassium could be obtained.[8]

In the first experiments the $NaOH \cdot 25H_2O$ solution was analyzed for caustic alkali, exactly as had been done before, by determining the weight of dried sodium chloride made from it. However, it was found that this method, as it had been carried out in the earlier work,[9] did not give the exact concentration of the solution, in spite of the agreement of the analyses. For this reason the first values obtained in confirmation of the new specific heat were discarded. The solution finally used for $NaOH \cdot 25H_2O$ was standardized not only by sodium chloride and sodium sulfate residues but also by titration with weight burets against hydrochloric acid standardized by silver chloride determinations.[10]

---

[7] *Cf.* Richards and Rowe, ***Proc. Am. Acad.,*** 49,183 (1913).

[8] The manufacturers reported that the potassium content varies from lot to lot and falls between 0.3 and 0.5% for the "c. P." material.

[9] *Cf.* ref. 2, p. 1883.

[10] The method of determining sodium as a chloride residue was investigated to find the error introduced by the retention of water. Some time ago attention was called to the difficulty of obtaining dry salts, especially anhydrous crystals [T. W. Richards, ***Proc. Am. Phil. Soc., 42, 28*** (1903)]. Sodium chloride crystals are notorious for their decrepitation on drying, a phenomenon depending on the bursting forth of included mother liquor.

In order to follow its behavior, a really anhydrous salt was prepared as the starting point. Pure sodium chloride, previously pulverized and dried in an oven, was fused in a covered platinum dish. The material thus obtained was neutral to phenolphthalein, methyl orange and methyl red. Weighed samples of this fused salt were dissolved and the solution evaporated in flasks in an oven at 100°, exactly as in the earlier analysis of sodium hydroxide by sodium chloride residue. Crystals about one cubic millimeter were formed. These gave an apparently constant weight after a few hours' heating at 150°. However, the salt thus dried without fusion was found to weigh 0.66 to 0.80% more than the really anhydrous substance (average 0.73%). The following modification

Analysis of $NaOH\cdot 25H_2O$ by evaporation as chloride showed the water content per mole to be 25.03 H_2O (the average of two analyses); by evaporation and fusion as sulfate, 25.06, 25.08, 25.07, average 25.07 H_2O; by titration with standard acid 25.08, 25.08, 25.09, average 25.08 H_2O.

The calorimetric experiment consisted in finding the weight of solution which showed exactly the same temperature rise as a given weight of water, when precisely the same quantity of heat was added.[11] A new "water equivalent" or weight of water fitting the conditions was determined as 556.42 g. of water at 18.00°, which corrected to vacuum was 557.01 g. in vacuo, as the average of six experiments. The "balancing weight," or thermally equivalent weight of $NaOH\cdot 25.08H_2O$ was 610.21 g. in vacuo, the average of five experiments (609.61, 609.61, 609.49, 609.72 and 609.67 g. in air) at the average temperature of 18.02". By use of the temperature coefficient determined by Richards and Gucker, the specific heat at 18.00' is calculated as 0.91280 for $NaOH\cdot 25.08H_2O$. This value may be accurately corrected to $NaOH\cdot 25.00H_2O$ by determining the value for the temperature coefficient for a dilution by a single molecule of water and by using the proper fraction of this value in Kirchhoff's Law.[12]

The specific heat of $NaOH\cdot 25.00H_2O$ then appears as 0.91262, to which should be added 0.00002 as the correction for cooling due to difference in evaporation of $NaOH\cdot 25H_2O$ solution and water, yielding 0.91264. One further small correction, that for the difference in heat capacity due to the trace of potassium, may be approximated by taking 0.15% (the approximate potassium content) of the difference in specific heats of sodium and potassium hydroxide solutions at this dilution (0 00007). The value 0.91271 is, therefore, the final value for $NaOH\cdot 25.00H_2O$ at 18.00°.

Besides this determination, a direct determination of the specific heat of $NaOH\cdot 101H_2O$ was made. This determination provided a corroboration of the specific heat values determined indirectly from heats of dilution. Analysis as sodium chloride residue, using the method of evaporation in an oven at 150–160°, showed the concentration of this solution to be $NaOH\cdot 101.08H_2O$.[13]

---

of the sodium chloride method was found to reduce to 0.05% or less the error of the result; it is not to be commended except for its rapidity. Indeed, the good result may be partly due to a compensation of errors. Nothing short of fusion will yield perfectly dry salt. If the sample solution of sodium chloride in a 125-cc. Erlenmeyer flask with anti-spattering bulb (such as is used in evaporating filtrates in flasks) is evaporated in an oven maintained at 150–160°, the salt is left as a powder which can be dried almost completely at 300–310°. As there is danger from spattering, the flask and bulb must be weighed together.

[11] Ref. 2, p. 1888.

[12] *Cf.* later paper for details of this correction.

[13] After this specific heat had been determined, it was found, as discussed in a previous footnote, that this method might produce an error of +0 05% in analysis which would correspond to +0.005% error in specific heat.

In this case the "water equivalent" of 596.01 g. *in vacuo* (average of four experiments) was found to be thermally equivalent to 614.84 g. *in vacuo* of solution (average of four determinations), the specific heat of which was, therefore, 0.96939 at 18.00° Correcting this to $NaOH \cdot 100H_2O$, we obtain 0.96904.

A rough measurement of the specific heat of a solution $NaOH \cdot 50.0H_2O$ also was made. This solution was adequately analyzed both by titration with acid and by evaporating the resulting salt in an oven at 160°, which process gave essentially identical results. The value obtained for the specific heat was 0.946 (507.7 g. of water being equivalent to 536.7 g. of solution). Minor temporary defects in the apparatus, chiefly tending to make the result too low, were experienced but the outcome could hardly be far from the truth.

These values are all essentially consistent with one another and with the heats of dilution found by Richards and Rowe. They are, however, all consistently higher than the final values calculated by these latter experimenters, who unfortunately had based their whole series on an erroneous value for $NaOH \cdot 10H_2O$, taken from older work[14] of others. The recent values are unquestionably far more trustworthy.

Since earlier values for the specific heat of sodium hydroxide solutions had been found to be in error, the question arose as to the correctness of specific heats of other hydroxide solutions. Accordingly, a solution of potassium hydroxide was prepared in a way similar to that used for the sodium hydroxide solutions.

This solution by titration against standardized hydrochloric acid was found to be $KOH \cdot 100H_2O$; by residue as KCl, $KOH \cdot 99.96H_2O$. The unimportant difference between these two results was doubtless chiefly due to water retained by the potassium chloride after rapid evaporation at 160°. Two more standardizations for the "water equivalent" (performed immediately after the $KOH \cdot 100H_2O$ solution had been examined) confirmed the value (found in the similar preceding experiments with $NaOH \cdot 101H_2O$) of 596.01 g. *in vacuo.* As the average of four experiments, 622.97 g. *in vacuo* of $KOH \cdot 100H_2O$ was found to be thermally equivalent. The specific heat of this solution, then, is 0.9567—a value which confirms exactly the early value for this dilute solution found by Richards and Rowe,[15] as well as their value found from heats of dilution.[16] Hence, evidently, the older results for potassium hydroxide were very nearly correct.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

[14] See Richards and Rowe, THIS JOURNAL, 43,781 (1921).

[15] Richards and Rowe, *Proc. Am. Acad.*, 49, 197 (1913).

[16] Richards and Rowe, THIS JOURNAL, 44, 694 (footnote27) (1922).

Summary

1. Several modifications and improvements made in the differential method for the determination of specific heats are presented.

2. The following values were found for specific heats at 18.00°. $NaOH\cdot 25H_2O$, 0.9127, thus confirming the recent high value found by Richards and Gucker; $NaOH\cdot 50H_2O$, 0.946; $NaOH\cdot 100H_2O$, 0.9690 and $KOH\cdot 100H_2O$, 0.9567.

St. Louis, Missouri

[Contribution from the Wolcott Gibbs Memorial Laboratory, Harvard University]

THE HEATS OF DILUTION OF SODIUM HYDROXIDE, ACETIC ACID AND SODIUM ACETATE, AND THEIR BEARING ON HEAT CAPACITIES AND HEAT OF NEUTRALIZATION[1]

By Theodore W. Richards and Frank T. Gucker, Jr.

Received September 18, 1928 Published March 6, 1929

Introduction

The most convenient and accurate way of studying heats of neutralization at successive concentrations is to determine the heat of neutralization at one concentration and the successive heats of dilution of the factors and products. In previous researches this method has been applied to several strong acids and bases, of which the heat of neutralization was found to *decrease* as the concentration decreased.[2] The present publication presents the first detailed study of an opposite case (acetic acid), in which the heat of neutralization was found to *increase* as the concentration decreased.

Method and Apparatus for Determining Heats of Dilution.—The principles involved in this research are essentially those of the previous dilution experiments.[3] Some differences in experimental detail, however, were applied and the calorimeter was greatly improved. The changes are fully described in the present paper.

The Calorimeter Proper

Figure 1 gives a general idea of the calorimetric apparatus. Two concentric platinum cans were used, the inner, C_2, having half the volume of the outer, C_1. (This assembly was designated Aa by Richards and Rowe.) The inner can always contained the solution and the outer can pure water. The liquids were agitated by two reciprocating stirrers, one, S_2, for the inner can and the other, S_1, for the annular space between the two. A somewhat elaborate mechanism was devised to keep the stirrers rigid (thus

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] Richards and Rowe, This Journal, 44, 704 (1922).

[3] Richards and Rowe, *ibid.*, 42, 1621 (1920); 43, 770 (1921).

avoiding irregular scraping against the sides of the cans). The stroke could be regulated so as to avoid splashing at the surface and still give the maximum permissible stirring.

The calorimeter proper was enclosed in a "submarine" jacket B, which was in turn submerged in a controllable outer water-bath **A,** described in detail later.

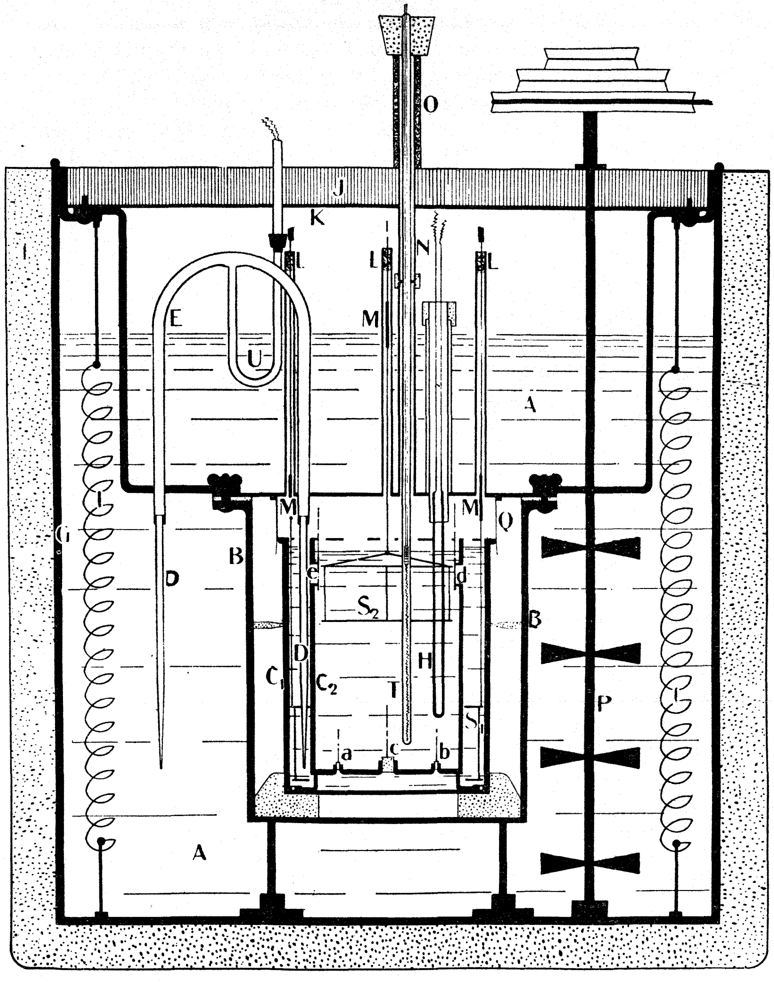


Fig. 1.—Calorimetric apparatus.

Valves between the Concentric Cans.—By opening five valves of different sizes in the inner can, C_2, its liquid could be mixed with that in C_1. The lower valves, a, b, were small platinum plugs, while the upper ones, d, e, were round pieces of thin sheet platinum. Each was sealed with a small quantity of paraffin wax melted into place. The large lower valve, c, was a rubber plug. All the valves were opened by wires passing out of the submarine through fine tubes. Small beads prevented them from being pulled above the level of the solution. The stirrers, moving at the same rate **but** in opposite directions, helped circulate the liquids and facilitated their mixing.

Thermometric Improvements.—The most important improvements in the present apparatus were (1) the substitution of a platinum resistance thermometer, T, for the mercury thermometer formerly employed to read the calorimeter temperature and (2) the use of a specially constructed thermel, DD, to compare the temperature of the outer water-bath (A) with that of the calorimeter itself. The first of these increased the thermometric sensitivity tenfold, while the second eliminated the necessity of reading two thermometers simultaneously in maintaining adiabatic conditions.

Platinum Resistance Thermometer.—The platinum resistance thermometer was of the Callendar four-lead type, made especially for the purpose by Leeds and Northrup. The pure platinum coil, 10 cm. long, mounted on mica and enclosed in a glass tube, was always completely beneath the level of the liquid in the calorimeter. Its constants were found by the Bureau of Standards (September, 1924) to be: $R_{0^\circ} = 25.301$ international ohms; $R_{100^\circ} = 35.151\omega$; $\delta = 1.51$.

A current of 2.5 m.a. was put through the thermometer coil in these standardizations. During the dilution experiments greater sensitivity was secured by using a current of 5 m.a. A half-dozen careful experiments showed that this increased current raised R_0 by 0.0015~. This change, though considerable, was constant and a corresponding correction was easily applied.

Resistance Bridge and its Thermostat.—In measuring the resistance of the thermometer coil, a high sensitivity bridge (of the same manufacture) also standardized by the Bureau (August, 1923) was used with many necessary precautions. At the completion of our experiments (April, 1928), a series of ice-points was taken with the thermometer and this bridge and a value $R_0 = 25.304\omega$ was obtained. This showed the magnitude of the change in the thermometer bridge system during the time it was in use. The average value $R_0 = 25.3025$~ was taken to compute the isothermal dilution temperatures, which are therefore fixed within ±0.015°. A change of 0.01° in this temperature causes a change as large as 1 joule only in the heat of dilution of sodium hydroxide (which has the largest temperature coefficient). It does not affect at all the ***temperature differences*** measured or the values of the temperature coefficients and heat capacities.

In order to make thermometer readings significant to 0.0001°, the bridge was enclosed in an efficient air-thermostat, kept constant within 0.01". The temperature of the resistance coils was undoubtedly yet more constant, since they were enclosed in the wooden and hard rubber box of the bridge.

The thermostat consisted of a large wooden box insulated outside by felt and provided inside with an adequate source of heat, a sensitive thermo-regulator and a fan. The dials and keys of the bridge were operated by extension rods running through the cover of the box.

The bridge was graduated to 0.0001 ohm and the deflections of a high sensitivity galvanometer gave the next decimal place by interpolation. A change of 0.00001 ohm in the resistance of the thermometer (corresponding to a temperature change of 0.0001°) caused a galvanometer deflection of 0.4 mm. External stray currents were kept out of the thermometer and galvanometer circuits by an equipotential shield and parasitic currents in the galvanometer circuit were canceled by a reversing switch.

The **Thermel.**—One of the chief requisites of precise calorimetry is the maintenance of a really adiabatic condition during an experiment. To compare the temperature of calorimeter and surrounding bath, a thermel connected directly to a galvanometer is more sensitive and convenient than two mercury thermometers. The ordinary glass-encased thermel, however, lags appreciably in registering the temperature difference. Accordingly, for this investigation the thermel was encased in platinum tubes, extending 10 mm. above the surface of the liquid. These were fastened with deKhotinsky cement into the glass tube E, forming the rest of the case. This thermel was compared by Dr. B. J. Mair and Dr. L. P. Hall with a glass-enclosed one similar to that used in the specific heat work[4] and found to respond about three times as rapidly to a change in temperature.

The element itself was of copper-constantan, made in two opposable sections of three couples each. The junctions were made in the usual manner[5] and staggered around the outside of a conical bunch, over a distance of 9 cm., in order to secure a "representative sample" of the temperature of the calorimeter over its whole height. This is one advantage of the thermel over the mercury thermometer, with its small bulb, especially when it is used as a zero instrument with changing temperatures. The cone of insulated wires fitted quite snugly into the metal case but to increase thermal conductivity, the interstices were filled with naphthalene.

The leads were carried inside a small water-proof rubber tube, over which was wound a double spiral strip of copper foil, which formed part of the equipotential shield (including the container of the outer bath, a copper plate under the reversing switch and another beneath the galvanometer). A double-pole double-throw switch, the only one in the circuit, served to reverse the galvanometer and so obtain the true deflection. The sensitivity of the thermel circuit was ample—0.0004° per mm. of scale.

Heating Coil.—A small heating coil H was used to adjust the initial temperature of the calorimeter. It was made from 28 cm. of number 30 B. and S. gage asbestos-insulated constantan wire, threaded through small brass tubing which was bent into a long U and heavily gold plated. The upper ends were cemented into a glass tube which fitted into one of the metal tubes in the "submarine" lid.

Outer Water-Bath.—This bath, of ample size, was thermally insulated by felt (F) and stirred by means of a three-stage propeller P, run at a high speed to insure thorough mixing. It was heated by means of two sets of coils of bare manganin wire, I, I, connected in parallel (each with a resistance of about 22 ohms) and supported on glass frames. To reduce the loss of heat by evaporation, a wooden cover (J) (lined with metal) was fitted over the bath.

Thermal Leakage.—To measure a temperature change with the accuracy of 0 0001°, heat leakage between the calorimeter and its surroundings must be made very small. The three main avenues of thermal leakage are (1) the air gap between calorimeter and jacket, (2) the solid connections bridging this space, and (3) evaporation from the surface of the calorimeter or condensation upon it.

(1) Calculation from Barry's[6] data for a nearly identical calorimeter system showed that an average thermal head of not more than ±0.003°, must be maintained during an experiment to avoid appreciable errors from leakage across the air gap. This condition was amply fulfilled during the experiments.

(2) The following precautions were taken to reduce conduction along the necessary solid connections between the calorimeter and the water-bath. The calorimeter was supported on small cork wedges and centered in the submarine jacket by small conical pieces of hard rubber. The platinum wires used to manipulate the valves were terminated just above the surface of the liquid and attached to insulating sections of waxed silk thread (dental floss). The wires supporting the stirrers were fastened into 2-cm. sections of glass tubing MMM to prevent metallic conduction along this avenue. In the small heating coil H the resistance wire was carried across the air gap, since its thermal conductivity was much less than that of the copper leads.

---

[4] Richards and Cucker, THIS JOURNAL, **47,** 1883 (1925).

[5] W. P. White, ibid., 36,2292 (1914).

[6] Barry, ibid., 44, 902 (1922).

Heat leakage from the room to the calorimeter over the leads to the temperature indicators was prevented by bringing them to the temperature of the water-bath. The thermel leads passed through a fine copper U-tube (U), which was immersed to the depth of 7 cm. in the water of the outer bath.[7] The protruding portion of the platinum thermometer stem was enclosed in a copper tube N, thermally insulated from the air of the room by a layer of cotton (O). Thus the whole stem was kept very near the temperature of the water-bath. Calculation showed that with the arrangements described the heat leakage by conduction was entirely negligible.

(3) Evaporation affords one of the most important minor possibilities of error in calorimetric work, often insufficiently regarded. One of its effects was pointed out long ago.[8] If the submarine jacket is cooler than the calorimeter, heat is lost from the latter much more rapidly than it is gained if the jacket is the same amount warmer, because in the first case water continuously distils from the calorimeter and condenses upon the jacket.

Barry[9] by careful experiments has also emphasized the importance of this effect. In the present apparatus the paraffined paper collar Q was designed to confine evaporation to the air space immediately above the calorimeter. Supposing this volume of air to be saturated at the beginning of an experiment, the error from additional evaporation, due to the slight change of temperature concerned, could hardly amount to over 0.00001°. Even this small error is at least partly eliminated by noting the temperature drift after the experiment proper. However, if the rise of temperature amounts to 4° (as in many thermochemical determinations) the error involved would be appreciable (0.0006°). If the usual open calorimeter were employed the error might be 0.003" or more.

The thin driving rods of the stirrers were of such cross sections that no significant volume of air was either drawn in or pumped out of the "submarine" during their alternating operation already mentioned. In addition they were packed with cotton (L) at the top of the tubes leading out of the submarine.

Heat Capacity of Apparatus.—The fixed heat capacity of the calorimetric apparatus was calculated as usual (from the weights and heat capacities of all the constituent parts) to be 18.46 (±0.3) cal. per degree, or 77.2 joules per degree (mayers).

The maximum uncertainty (0.03%) of the total heat capacity of the calorimetric system (including the liquids) was unimportant for the present purpose but should be considered in cases where a percentage accuracy of this order is sought.

Materials and Solutions.—The materials were purified and standardized in much the same manner as for the previous research.[4] The most difficult problem was the sodium hydroxide. It was obtained by crystallization from very concentrated solutions with many precautions. The method of standardization of this alkali used in the specific heat experiments and in the first series of dilution experiments has since been shown to be insufficiently exact for the present purpose. Indeed, this would have been suspected at the time, except for the fact that the comparison with "constant boiling" hydrochloric acid and the weighing of sodium chloride had given an identical outcome. The former method, however, is not always trustworthy; the latter is almost certain to yield too high results. It now appears[10] that sodium chloride ob-

---

[7] A similar procedure was adopted by Williams and Daniels, THIS JOURNAL, 46, 905 (1924).

[8] Richards and Burgess, *ibid.*, 32,449 (1910).

[9] Barry, *ibid.*, 44, 899 (1922). W. P. White, likewise, has entirely appreciated the necessity of preventing evaporation.

[10] Richards and Hall, *ibid.*, **51,** 707 (1929). Nearly all the present work was done in 1924–1925 and has been awaiting publication until the subsequent confirmatory work of Richards and Hall could be finished.

tained by evaporation in the particular manner described in our above-mentioned research regularly retains 0.7% of water. The first analysis of the $NaOH\cdot 25H_2O$ solution was, therefore, in error by $0.20H_2O$. All the concentrations in the previous paper are here corrected for this source of error. The final corrected estimate of the concentration of sodium hydroxide employed in the first series of the present work was $NaOH\cdot 25.31H_2O$. That used for the second series was titrated against hydrochloric acid solution, standardized by silver chloride and hence requires no correction.[11]

The acetic acid was a very pure specimen of the glacial acid, which was further purified by three recrystallizations. The composition of the standard acetic acid solution, analyzed by titration against $NaOH\cdot 25.31H_2O$, was found to be $HC_2H_3O_2\cdot 25.17H_2O$.

We wish to thank Dr. L. P. Hall for the laborious recalculation of the first series of sodium hydroxide dilution experiments and the acetic acid dilution experiments to the true concentrations.

The sodium acetate was a "chemically pure" sample from a responsible firm; it was recrystallized twice from a clear solution as trihydrate and duly centrifuged, etc. The standard solution was made at first somewhat too concentrated; after careful analysis it was diluted quantitatively to the concentration $NaC_2H_3O_2\cdot 24.99H_2O$. The analysis was conducted by evaporation at 100° and heating to constant weight at 200°. Later experiments (converting the acetate into the anhydrous sulfate in the usual way) showed that the porous powder thus prepared retained only 0.1% of water. This error would affect the heat of dilution by less than 1 joule at the greatest concentration involved and no corrections were made to the observed values.

In calculating the concentrations of these solutions the following atomic weights were used: $H = 1.008$; $O = 16.000$; $Na = 22.997$; $C = 12.000$ and $S = 32.064$.

The initial solutions (about $25H_2O$) were kept in stock bottles in the manner already described.[4] For each quantitative dilution the required amounts of solution and of water were weighed out (within 0.01%). Since in the thermochemical determinations the dilutions were made in successive steps, the product of one experiment served as a factor in the next. The products were carefully preserved and protected from evaporation, so that it was unnecessary to analyze the successive more dilute solutions.

Experimental Procedure

The technique of experimentation was planned so as to conserve time and avoid evaporation of the weighed solutions. Description of the individual steps would be helpful to any one repeating the work, but would require too much space for the present record. When all was in place the temperature of the calorimeter system was slowly raised to the desired initial temperature by passing a current through the inner heating coil. The temperature of the outer bath was then made the same (± 0.003"). Finally, the inner heating coil was disconnected and the apparatus kept for at least five minutes under careful adiabatic control before the first accurate reading of the resistance thermometer.

---

[11] Richards and Hall (ref. 10), verified these conclusions by making an entirely new solution of sodium hydroxide, analyzing it by titration against a hydrochloric acid solution standardized by precipitation of silver chloride and determining its specific heat with great accuracy. This value exactly agreed with that found by us previously, when allowance was made for the 0.7% of water held by sodium chloride obtained by evaporation. There can thus be no reasonable doubt of the true concentration of sodium hydroxide solution formerly used by us, and of our present solution.

The time of completing the first reading was recorded to the nearest quarter of a minute. Pour minutes later a second reading was made, followed by a third, after an equal interval of time. If the temperature trend during these two periods was sufficiently constant, the experiment was started by pulling out the two platinum valves, a,b, (Fig. 1).[12] This was done at the beginning of an upstroke of the inner stirrer so that the first mixing would occur in the center of the apparatus where it was least likely to cause an uneven temperature on the surface of the calorimeters. The temperature change in the latter (as indicated by the thermel) was carefully paralleled in the outside bath by appropriate heating, or cooling by a small stream of ice water dropping directly over the stirrer. The thermal head for the first two minutes was usually about *0.015°, but for the rest of the experiment it was less than ±0.003°. The average temperature of the bath always was kept slightly higher than that of the calorimeter. When about three minutes had passed and the mixing was practically complete, the other valves were opened. Three minutes later the resistance thermometer was again read to determine the temperature change during the experiment. After eight minutes more a final reading was made to determine the temperature trend after the experiment. The temperature of the bridge thermostat was noted after every thermometer reading in order to be sure that it functioned properly.

A Typical Dilution Experiment.—The full data of a typical experiment will show the method of calculating the true rise of temperature and the amount of heat evolved or absorbed in the reaction.

The temperature drift in eight minutes was equivalent to -0.00009 ohm before the experiment; afterward, -0.00005 ohm. The mean drift was, therefore, -0.00007 ohm during eight minutes (the time of the experiment). Hence the change in resistance during the experiment, corrected for this trend, was $+0.00725 - (-0.00007) = +0.00732$ ohm.

The change of resistance was translated into temperature change by means of a difference formula derived from the familiar Callendar equation by Mueller of the Bureau of Standards.[13] It may be written AT = $\Delta\phi R$. The factor ϕ depends upon the mean temperature of the experiment, increasing 0.03% for every degree of temperature rise; in this case it was 10.0613, so that the change in temperature AT = 0.0737'. The final temperature of the experiment was 20.09".

The quantity of heat absorbed in any single experiment (Ah) was calculated from the temperature change and the heat capacity of the system by the equation $Ah = -\Delta T c_p$. c_p is the sum of the heat capacities (under constant pressure) of the factors and that of the apparatus. The heat

---

[12] When the temperature change was very small (in the experiments at great dilution) the mixing was effected more rapidly by opening the large valves, d, e, first.

[13] Bureau of Standards Bulletin No. 9, reprint 200.

TABLE I

EXPERIMENT No. 4

May 7, 1925. Dilution: $HC_2H_3O_2 \cdot 25H_2O + 25H_2O = HC_2H_3O_2 \cdot 50H_2O$.

Calorimeters + solution + water, 1557.98 g. Calorimeters + solution, 1008.56 g. Water, 549.42 g. Calorimeters, 387.12 g. Solution 621.44 g.

Resistance Readings of a Single Experiment

Time	Δt, minutes	Bridge reading, ohms[a, b]	Galv. swing, cm.	Corr. reading, ohms[c]	ΔR, ohms
10:14.0		27.2957 (2)	+0.33		
		27.2958 (2)	−0.11	27 29671	
	6.0				−0.00007
10 20 0		27.2957 (2)	+0.04		
		27.2958 (2)	−0.38	27.29564	
	4 0				−0.00004
10.24 0[d]		27.2956 (1)	+0.34		
		27.2957 (2)	−0.11	27.29560	
	8 0				+0.00725
10.32.0		27 3028 (2)	+0.15		
		27.3029 (1)	−0.27	27.30285	
	8.0				−0.00005
10:40		27.3027 (2)	+0.32		
		27.3028 (2)	−0.10	27.30280	

[a] The bridge thermostat read exactly 25.00" before and after the experiment. At no time was the thermal head greater than ±0.008°.

[b] The calibration corrections for the 0.000 R coils (in parentheses) were necessary to interpolate the fifth place correctly, since the change was not exactly 0.0001 ohm in each case.

[c] The interpolated values are corrected by adding the calibration corrections to all coils changed during an experiment (here, 0. R to 0.000 R inclusive).

[d] The upper platinum valves, d, e, were opened at 10:24.0 to start the experiment and the lower rubber valve, c, at 10:27 to ensure complete mixing.

capacity of the factors was determined by multiplying the weight of each by its heat capacity per gram, at the mean temperature of the experiment. The values for the heat capacities of the concentrated solutions were taken from the work of Richards and Gucker,[4] as duly corrected by Richards and Hall.[10]

In this particular experiment (using c_2 to signify the heat capacity of the dilute acetic acid and c_1 that of the water used for further dilution)

$$c_2 = 622.09 \times 3.9915 = 2483.1 \text{ mayers (joules per degree)}$$
$$c_1 = 550.00 \times 4.1836 = 2301.0 \text{ mayers (joules per degree)}$$
$$c_a = 77.2 \text{ mayers (joules per degree)}$$
$$c_p = (c_2 + c_1 + c_a) = 4861.3 \text{ mayers (joules per degree)}$$

Hence

$$Ah = - A Tc, = -(0.737) \times (4861.3) = -358.3 \text{ joules.}$$

The heat absorbed (AH) by the dilution of a mole of solute was obtained by dividing the heat absorbed in any experiment *(Ah)* by the number (N) of moles of solute used.[14]

In this case N = 1.2114 and

$$AH = \Delta h/N = -(358.3)/(1.2114) = -295.8 \text{ j}.$$

This value corresponds to isothermal dilution at the final temperature, 20.09°, since the heat capacity of the factors was used in the calculation.[15]

Prom the experimental values of AH at approximately 16 and 20° its temperature coefficient was obtained and used to correct the results to exactly 16 and 20°.

Since the data necessary for these calculations are too bulky for publication in complete form, only the results will be presented.

The difference between parallel experiments often was less than 0.5 joule, which corresponded to an error in temperature reading (AT) of about 0.0001". Occasionally (especially in the case of sodium acetate) the difference amounted to four times as much; in such cases more determinations were made. The sodium acetate experiments were chronologically the first; the better agreement in the other cases is to be ascribed to increased experimental efficiency.

Three blank experiments were carried out to determine any temperature change which resulted from pulling out the plugs and mixing the contents of the two calorimeters. The actual experimental conditions were duplicated as closely as possible. In the first case each calorimeter contained water; in the others a $NaOH\cdot 800H_2O$ solution. The results were: $AT = -0.0000_8°$, $\pm 0.0000_0°$, $-0.0000_5°$, making an average of $-0.0000_4°$. This quantity is beyond the limit of experimental accuracy and the experiments show that no appreciable error can have been introduced in mixing the solution.

With sodium acetate the dilutions were carried to $51H_2O$, $101H_2O$, $201H_2O$, etc., in order to measure directly values required to calculate heats of neutralization. The calculation of the heat capacities per gram is discussed later.

The calculations were carried to two doubtful places and only the final results rounded off in order to prevent cumulative errors.

[14] Attention should be called to a difference between the symbols used in this paper and in previous publications from this Laboratory. Formerly (in conformity with usual practice) U was used to denote diminution of total energy during a reaction (or, where there is no significant change in volume, the heat *evolved).* Unfortunately U recently has been taken to mean the (unknown) total internal energy of a system. — AU in this new notation is identical in meaning to the old U, and AH means heat ***absorbed*** per mole under constant pressure. The new notation, which is now most frequently employed in America, is used herewith; but the whole subject seems to need revision. At present the notation of chemical thermodynamics is in dire confusion, especially because of changes of sign.

[15] Richards, **THIS JOURNAL,** 25,209 (1903).

Note on Sodium Hydroxide.—Two series of determinations were made on the sodium hydroxide solutions. The first series was brought to an abrupt close by a very hot spell in June, 1925. Because of the sudden change of the heat of dilution at the last stage, extrapolation to zero concentration seemed of doubtful value without additional knowledge. Accordingly, in January and February, 1928, the second series was carried out and showed that the heat of dilution actually changed sign at this point. The curve was followed to $NaOH \cdot 3200H_2O$ because, although the percentage accuracy of these figures is not great, they reduce the uncertainty in the final extrapolation to zero concentration.

The diluting water was distilled, then boiled for five to ten minutes to drive out most of the dissolved air and carbon dioxide. Nevertheless, the presence of a minute trace of carbon dioxide would cause the evolution of a relatively large heat of neutralization during the experiment. Tests with barium hydroxide solution gave no precipitate, showing (by comparison with a standard sodium carbonate solution) that the water contained less than 0.00004% carbon dioxide (by weight). The $NaOH \cdot 3200H_2O$ solution, however, showed about 0.00008% of sodium carbonate, which had accumulated during the five dilutions. Estimating that one-eighth of this came from the diluting water and the rest from the air of the room, during the weighing and handling of the solution, a correction, amounting to 0.0002° in each dilution, was applied to the observed heats of dilution in computing the final values and extrapolating to zero concentration. Had this difficulty been fully appreciated at the beginning of the experiments, it might have been avoided by adding to the diluting water enough sodium hydroxide or barium hydroxide to react with the $CO_3^=$. The very dilute carbonate solution resulting would probably, as a diluent, be indistinguishable within the limit of accuracy of the present apparatus, from absolutely pure water. To use pure water (containing an amount of carbon dioxide negligible in diluting hydroxide solutions) in such a calorimetric apparatus would be almost impossible.

Heat Capacities.—Knowing the heat capacities of the initial solutions[16] and the heats of dilution at 16 and 20°, the heat capacities of the products of each dilution were calculated by the principle commonly known as Kirchhoff's Law.[17]

---

[16] Richards and Cucker, **THIS** JOURNAL, *47*, 1883 (*1925*).

[17] $(AH' - \Delta H)/(T' - T) = \Delta C_p$, where $\Delta C_p = C'_p - C_p$. Here C'_p = total heat capacity of products and C_p = total heat capacity of factors. ΔC_p refers to the change in heat capacity at the mean temperature $(T' + T)/2$, in this case *18.00°*. Since, however, the change of ΔC_p with temperature may probably be considered negligible over a 4° interval, the same value of AC_p was used in calculating specific heats at 16, *18* and *20°*.

It is interesting to note that Person in *1851* [*Ann. chim. phys.*, [3] *27, 250 (1849)*; **[3]** *33, 437* (1851)], from an inductive study of his data on heats of solution and specific

These calculations, like the dilution experiments, were carried out in steps, the heat capacities calculated from one dilution becoming those of the factors of the next. The method is illustrated by the following example involving sodium hydroxide at 16.00°.

Factors	Mol. wt.	c_p (per gram), m.	C_p (per mole), m.	ΔC_p, m.
$NaOH \cdot 25H_2O$	490.41 g.	3.8132	1870.03	
$+ 25H_2O$	450.40 g.	4.1837	1884.34	
			3754.4	−31.4

Product	C_p (per mole), m.	Mol. wt.	c_p (per gram), m.
$NaOH \cdot 50H_2O$	3725.0	940.81 g.	3.9572

From these values in the absolute system those in the 20° calorie system are easily computed by dividing by 4.1805 (the absolute heat capacity of a gram of water at 20°). For the more convenient use of others these heat capacities were reduced to exactly even molal concentrations—for example, those of $25.31H_2O$ to exactly $25H_2O$. In the following tables, II, III and IV, all these data are brought together. They (as well as the other final data in this paper) are, of course, corrected for all known errors.

From the data obtained tables were prepared giving the heats of dilution and the change of heat capacities during dilution of the different solutions of the substances studied (see Tables V, VI and VII).

TABLE II
SODIUM HYDROXIDE

c_p[a] in mayers (joules/degree) 16°	18°	20°	Solution	c_p[a] in calories$_{20°}$/degree 16°	18°	20°
3.8132	3.8170	3.8213	$NaOH \cdot 25H_2O$	0.91214	0.91305	0.91408
3.9572	3.9584	3.9599	$NaOH \cdot 50H_2O$	.94659	.94687	.94723
4.0529	4.0526	4.0527	$NaOH \cdot 100H_2O$	,96948	.96941	.96943
4.1127	4.1117	4.1110	$NaOH \cdot 200H_2O$	.98378	.98354	.98338
4.1467	4.1453	4.1442	$NaOH \cdot 400H_2O$	.99191	.99158	.99132
4.1648	4.1633	4.1620	$NaOH \cdot 800H_2O$	.99624	.99589	.99557
4.1741	4.1725	4.1711	$NaOH \cdot 1600H_2O$	.99847	.99809	.99775

[a] Heat capacity (at constant pressure) per gram of substance.

---

heats, discovered this same relationship and expressed it in a mathematical equation which can be shown to be identical with the Kirchhoff equation. Since his work predated that of Kirchhoff [Ostwald's "Klassiker der Exakten Wissenschaften," No. 101, reprinted from Kirchhoff, *Pogg. Ann.*, 103, 77, 206 (1858); 106, 322 (1859)] by seven years, his priority should be recognized and the principle renamed the "Person-Kirchhoff Law." This would also obviate any confusion between the law just mentioned and the other laws of Kirchhoff in the domain of pure physics.

Other referencesto the use of this equation follow: Winkelmann, *Ann. Phys. Chem.*, 149, 1 (1873); Dupre, *Proc.* Roy. *Soc.*, 20, 336 (1873); Berthelot, *Ann. chim. Phys.*, [5] *4*, 21 (1875); Pickering, *J. Chem. Soc.*, *57*, *88* (1890); Richards and Lamb, *Proc.* Am. *Acad.*, 40, 678 (1905); Brönsted, *Z. physik. Chem.*, *56*, 577–680 (1906); Tucker, *Phil. Trans.*, [A] 215,319 (1915); Richards and Rowe, ref. 2

TABLE III

ACETIC ACID

$c_p{}^a$ in mayers (joules/degree)				$c_p{}^a$ in calories$_{20°}$/degree		
16°	18°	20°	Solution	16°	18°	20°
3.9900	3.9901	3.9920	$HAc\cdot 25H_2O$	0.95443	0.95446	0.95491
4.0869	4.0853	4.0856	$HAc\cdot 50H_2O$	.97740	.97723	.97730
4.1348	4.1336	4.1330	$HAc\cdot 100H_2O$	.98907	.98878	.98864
4.1592	4.1576	4.1567	$HAc\cdot 200H_2O$	.99491	.99452	.99431
4.1714	4.1698	4.1686	$HAc\cdot 400H_2O$	.99782	.99744	.99715
4.1774	4.1757	4.1743	$HAc\cdot 800H_2O$	.99926	.99885	.99852

[a] Heat capacity (at constant pressure) per gram of substance.

TABLE IV

SODIUM ACETATE

$c_p{}^a$ in mayers (joules/degree)				$c_p{}^a$ in calories$_{20°}$/degree		
16°	18°	20°	Solution	16°	18°	20°
3.7653	3.7680	3.7712	$NaAc\cdot 25H_2O$	0.90068	0.90133	0.90209
3.9348	3.9355	3.9365	$NaAc\cdot 51H_2O$	.94123	.94140	.94163
4.0447	4.0443	4.0441	$NaAc\cdot 101H_2O$	.96752	.96742	.96737
4.1091	4.1080	4.1075	$NaAc\cdot 201H_2O$	,98292	.98268	.98254
4.1450	4.1435	4.1425	$NaAc\cdot 401H_2O$	.99151	.99115	.99091
4.1637	4.1620	4.1608	$NaAc\cdot 801H_2O$	.99598	.99558	.99529
4.1734	4.1717	4.1704	$NaAc\cdot 1601H_2O$	.99830	.99790	.99758

[a] Heat capacity (at constant pressure) per gram of substance.

The values for infinite dilution were obtained by graphical extrapolation with a Berkeley flexible ruler. The curve for acetic acid was nearly a straight line, which made extrapolation easy. The sodium acetate curve was regular but difficult to extrapolate because it was inclined so obliquely to the axis. The dilute portion of the sodium hydroxide curve was similar to that of sodium acetate.

Considering all the results obtained, including those for the dilution of sodium hydroxide carried out after an interval of two years, it seems probable that the average values for A T are not more than 0.0002° from the true value. In considering the accuracy of the tabulated results and the extrapolations, however, it must be remembered that the error in the molal heat of dilution is doubled with each step, because the molal heat capacity is doubled. This cumulation of errors is inevitable and should be clearly borne in mind.

The possible error in the molal heat of dilution is increased from about 1.6 j. (in the dilution from $MX\cdot 50$ to $MX\cdot 100H_2O$) to almost 24 j. (in the dilution from $MX\cdot 800$ to $MX\cdot 1600H_2O$). The possible accumulated error in the value for the dilution $MX\cdot 50$ to $MX\cdot 1600$ is therefore about 48 j., and that in any extrapolation to zero concentration might amount to as much as 75 or 100 j.

In the sodium hydroxide solutions the uncertainty of the carbon dioxide correction increases the possible error to 0.0003°, or a possible uncertainty of 150 j. in the extrapolation. The fact that, plotting on a large scale, smooth curves are obtained, makes it probable that the *actual* errors are not as large as the *possible* errors just discussed.

TABLE V

HEATS OF DILUTION (CORRECTED)
Sodium Hydroxide

Moles of water/mole of NaOH		$\Delta H_{16°}$[a]		$\Delta H_{20°}$[a]		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	50	587	140.5	461	104.9	−31.4	− 7.5
25	100	1004	240.2	767	183.5	−59.2	−14.2
25	200[b]	1197	285.9	889	212.7	−77.0	−18.4
25	400[b]	1247	298.4	902	215.9	−86.7	−20.7
25	800	1273	292.6	860	205.7	−91.5	−21.9
25	1600	1180	282.3	803	192.1	−95.0	−22.7
25	3200	[1132][c]	[270.8]	749	228.7	[−95.91	....
25	∞	[1071]	...	[682]	[163.1]	[−97.41	[−23 2]

[a] All results are corrected for 0.00001% of CO_2 in the diluting water.

[b] The values here recorded are the average of the two series.

[c] Bracketed figures are obtained by extrapolation.

TABLE VI

HEATS OF DILUTION (CORRECTED)
Acetic Acid

Moles of water/mole of HAc		$\Delta H_{16°}$		$\Delta H_{20°}$		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	50	−316.1	− 75.6	−296.5	− 71.0	4.9	1.16
25	100	−492.4	−117.7	−461.2	−110.4	7.8	1.95
25	200	−580.7	−138.9	−544.8	−130.4	9.0	2.23
25	400	−624.5	−149.3	−586.9	−140.5	9.4	2.33
25	800	−637.0	−152.3	−608.6	−145.6	7.1	1.53
25	∞	[−653]	[−156]	[−630]	[−151]	[5.8]	[1.4]

TABLE VII

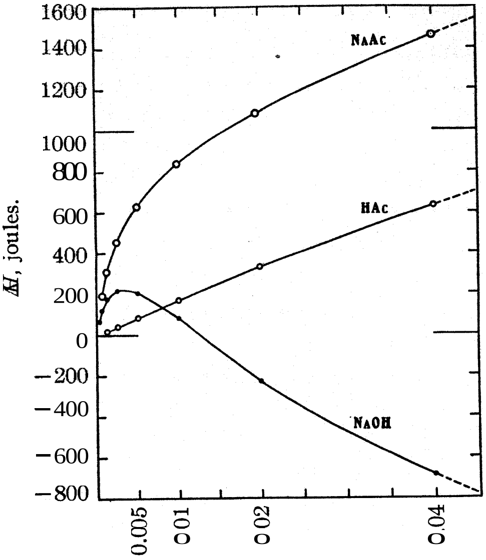
HEATS OF DILUTION (CORRECTED)
Sodium Acetate

Moles of water/mole of NaAc		ΔH_{16}		$\Delta H_{20°}$		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	51	−277.9	− 66.4	− 382.9	− 91.6	−26.3	− 6.3
25	101	−450.8	−107.7	− 623.3	−149.1	−43	−10.4
25	201	−616	−147.2	− 831	−198.6	−54	−12.9
25	401	−766	−183.1	−1007	−241	−60	−14.5
25	801	−894	−213	−1156	−276	−65	−15.7
25	1601	−991	−238	−1275	−312	−71	−17.0
25	∞	[−1152]	[−276]	[−1464]	[−351]	[−78]	[−19]

The heats of dilution in Tables V, VI and VII are plotted in Fig. 2 in such a way as to be most directly comparable.

Since at zero concentration all heats of dilution must approach zero, the curves are drawn from a common origin. The concentration is plotted in moles of solute per mole of water as abscissa, while as ordinate is plotted the heat absorbed in going *from* zero concentration to that represented by the abscissa of the point.

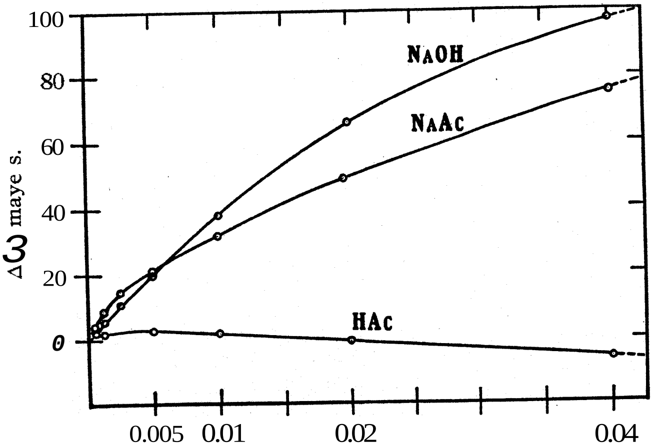
It is interesting to see that in every case at the lowest concentration heat is given out by further dilution. Lange and Messner[18] in their recent study of extremely dilute solutions have found this to be a general rule.



Concentration, moles of substance per mole of water.

Fig. 2.—Heats of dilution.

The temperature coefficients of the heats of dilution, which represent the change of heat capacity with change of concentration, were plotted in Fig. 3. Here also the curves are drawn from a common origin, to be more directly comparable. The abscissas again represent concentration and the ordinates the *gain* in heat capacity, per mole of solute, in going from zero concentration to that repre-



Concentration, moles of substance per mole of water.

Fig. 3.—Change of heat capacity (in mayers).

---

[18] Lange and Messner, *Naturwissenschaften*, 15, 521 (1927).

sented by the abscissa. The curves for sodium hydroxide and sodium acetate are regular and similar. That of acetic acid is more interesting. In the more concentrated range its slope is opposite to that of the others, but at a concentration of about $HC_2H_3O_2 \cdot 600H_2O$ it changes sign and then behaves normally.

All the solutions of acids, bases and salts studied by Richards and Rowel[g] (including sodium hydroxide) showed a diminution in heat capacity on dilution. This is seen to be true also of sodium acetate and dilute acetic acid solutions. Concentrated acetic acid solutions, however, when diluted show an increase in heat capacity.

The heats of dilution given in Tables V–VII can be used to calculate the change with concentration of the heat of neutralization of sodium hydroxide and acetic acid, by the familiar addition of thermochemical equations.[20]

Knowing the heat of neutralization at any single concentration, the whole course of the curve is fixed. The best value available in the literature is $NaOH \cdot 200H_2O + HC_2H_3O_2 \cdot 200H_2O = NaC_2H_3O_2 \cdot 401H_2O + 13.48$ Cal.[21] Our dilution data show that the heat of neutralization at infinite dilution is 0.04 cal. greater than this, or 13.52 cal. This result is not far below the extrapolated value of 13.62 found for the neutralization of strong acids. It seems safe to conclude that the hea' evolved by the reaction $H^+ + OH^- = H_2O$ is not very far from 13.6 cal. The weakest link in this chain is the heat of neutralization of acetic acid at ordinary concentrations, which will be taken up in a paper by Dr. B. J. Mair and one of us.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

This paper presents new data on the specific heats and heats of dilution at 16 and 20° of sodium acetate, sodium hydroxide and acetic acid. These data are necessary in order to compute the heats of neutralization involved

---

[19] Richards and Rowe, THIS JOURNAL, 43,788 ff. (1921).

[20] Cf. Richards and Rowe, *ibid.*, 44, 700 (1922).

[21] Thomsen found the heat of neutralization of hydrochloric acid at about 18° to be 13.74 Cal. and that of acetic acid to be 0.34 Cal. less, a differenceof 2.5%. The factors in both of these reactions contain $200H_2O$. Richards and Rowe found 57.75 kilojoules for the heat of neutralization of hydrochloric acid at 20° (making a small correction for the error in analysis of the sodium hydroxide used by them). Subtracting 2.5% from this gives 56.3 kilojoules or 13.47 Cal. as the heat of neutralization of acetic acid reduced to the same standard. Mathews and Germann [*J. Phys. Chem.*, 15, 75 (1911)] find that the heat of neutralization at 18° of 0.25 *N* $HC_2H_3O_2$ and NaOH is 2.3% less than that of HCl at the same concentration. This would give a value of 56.4 kj., or 13.49 Cal., at 20°, on our standard. The average of these is 13.48 Cal.

at various concentrations. The apparatus has been improved and all temperature measurements made by a platinum resistance thermometer. A careful study of the possible errors has been made and suitable corrections applied for them.

It has been found that although all the other heats of neutralization studied in this way *decrease* as the concentration of the reagents is diminished, that for acetic acid (which is distinctly less than those of stronger acids) *increases* as the solutions become more dilute. Apparently, however, they tend toward the same value at infinite dilution, about 13.6 Cal. (or 56.8 kilojoules), which would appear to be the most probable value for the heat of the reaction $H^+ + OH^- = H_2O$. A more exact evaluation will be found in a later paper of this series.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

HEATS OF DILUTION AND HEAT CAPACITIES OF HYDROCHLORIC ACID SOLUTIONS[1]

BY T. W. RICHARDS, B. J. MAIR AND L. P. HALL

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

Introduction

Since the publication of preliminary data of the specific heats and heats of dilution of hydrochloric acid solutions by Richards and Rowe,[2] more accurate methods for the determination of these data have been developed in this Laboratory.[3] With the aid of these new methods and apparatus the specific heats of hydrochloric acid solutions at various concentrations have been obtained directly and also indirectly from the heats of dilution at 16 and 20°.[4]

Specific Heats of Hydrochloric Acid Solutions

The specific heats of hydrochloric acid solutions at three concentrations were determined in a manner identical with that previously described.[6] A variable but small error may have been caused by the action of the hydrochloric acid on the gold-plated heating coil, particularly at the soldered connections. At first a celluloid cement was used to coat these sections. In spite of this precaution the acid solution was able to attack the solder

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior authors.

[2] Richards and Rowe, THIS JOURNAL, 42,1621 (1920).

[3] (a) Richards and Gucker, *ibid.*, 47, 1876 (1925); (b) 51, 712 (1929).

[4] The relationship between the temperature coefficient of the heat of dilution and the heat capacity of the factors and products $(AH' - \Delta H)/(T' - T) = \Delta C_p$ generally known as Kirchhoff's Law was used for this purpose (ref. 2).

[5] Richards and Hall, THIS JOURNAL, 51,707 (1929).

very slowly. A thin coating of paraffin was found to be more effective than the cement. Heat evolved by corrosion must have been slight even in the case of the most concentrated solution and would tend to lower the results to a very small extent.

The water equivalent in all of the determinations with hydrochloric acid was 556.71 g. in *vacuo*. A solution of redistilled hydrochloric acid was titrated against $NaOH\cdot 25.08H_2O$ with weight burets and found to be $HCl\cdot 24.96H_2O$ and the same value was found by analysis as silver chloride.

WEIGHTS OF $HCl\cdot 24.96H_2O$ EQUIVALENT TO 556.71 G. OF H_2O

	16.00° *g. in vacuo*		18.00° *g. in vacuo*		20.00° *g. in vacuo*
	636.42		**635.15**		**634.87**
	635.99		**635.36**		**634.62**
			635.25		
	636.29		**635.24**		**634.75**
Av.	**636.23**	Av.	**635.25**	Av.	**634.74**
Sp. ht.	**0.87501**	Sp. ht.	**0.87636**	Sp. ht.	**0.87707**

When these values for specific heats are corrected to $HCl\cdot 25.00H_2O$ by means of the Person-Kirchhoff Law, the following result: at 16°, 0.87518; at 18°, 0.87653; at 20°, 0.87724. These values are subject to a correction of 0.00002 to 0.00004 resulting from differences in evaporation of solution and water.

A solution of redistilled hydrochloric acid was adjusted to about $HCl\cdot 50H_2O$ and analyzed by the silver chloride method as $HCl\cdot 49.99H_2O$. Its specific heat at 18° was found to be 0.9337 as the mean of two experiments requiring 596.24 and 596.18 g. in *vacuo* of the acid.

937.01 g. of this acid was diluted with 901.10 g. of water to make a solution of $HCl\cdot 100H_2O$. From three experiments (576.90 g., 576.90 g. and 576.75 g., all in *vacuo)* the specific heat at 18.03' was found to be 0.9651.

Determination of Heats of Dilution

The apparatus and experimental procedure used in these experiments was essentially that described in a recent paper.[3b] A few minor modifications in apparatus were made. Owing to the solvent action of hydrochloric acid on the gold-plated brass heating coil formerly used to adjust the initial temperature, a simple though adequate heating coil was made from constantan wire (No. **30** B. and S.) enclosed in a thin-walled glass capillary.

One of the most troublesome experimental difficulties encountered was the erratic heating effect arising from the occasional contact of the stirrers with the sides of the calorimeter cans. This difficulty was considerably decreased by bracing the supporting rods of the stirrers and by reducing their width slightly. Further reduction of this heating effect was accomplished by binding the edges of the stirrer in a few places with waxed silk thread.

A new "all copper circuit" galvanometer of high sensitivity was used in conjunction with the platinum resistance thermometer to eliminate thermo-electric currents frequently found in galvanometers of the silver suspension type.

The heat capacity of the apparatus was calculated from the heat capacity of its constituent parts as 76.4 (±3) mayers. Since the total heat capacity of the system with solution was about 5000 mayers, an error of 3 mayers corresponds to an error in total heat capacity of only 0.06%, which is within the accuracy of the rest of the method.

Hydrochloric acid, doubly distilled, using a quartz condenser, was diluted to approximately $HCl{\cdot}25H_2O$. Two solutions were used: the first by analysis as silver chloride was of the concentration $HCl{\cdot}24.95H_2O$; the second, $HCl{\cdot}24.98H_2O$. The first solution was used for experiments at 20° only, while the second was used one year later at both 16 and 20°, after considerable experience had been gained with the apparatus.

No attempt will be made to present the necessary data for all of the calculations. The same general methods of calculation were used here as described in the previous article in this series[6] Two series of dilution experiments were performed with the hydrochloric acid solutions.

The summaries of results are given in Tables I and II.

TABLE I

HEAT CAPACITY PER GRAM OF SOLUTION

Mayers			Solution	20° Calories		
16°	18°	20°		16°	18°	20°
3.6615	3.6657	3.6673	$HCl{\cdot}25H_2O$	0.8758	0.8769	0.8772
3.9017	3.9031	3.9031	$HCl{\cdot}50H_2O$	.9332	.9336	.9336
4.0369	4.0367	4.0361	$HCl{\cdot}100H_2O$	.9656	.9656	.9654
4.1062	4.1072	4.1082	$HCl{\cdot}200H_2O$	.9822	.9822	.9822
4.1452	4.1439	4.1426	$HCl{\cdot}400H_2O$	.9916	.9912	.9909
4.1643	4.1628	4.1614	$HCl{\cdot}800H_2O$	.9961	.9958	.9954

TABLE II

HEATS OF DILUTION OF $HCl{\cdot}25H_2O$

	$\Delta H_{16°}$		$\Delta H_{20°}$		ΔC_p	
Product	Joules	Cal.	Joules	Cal.	J/°C.	Cal./°C.
$HCl{\cdot}50H_2O$	−919	−220	−959	−229	−10.0	−2.4
$HCl{\cdot}100H_2O$	−1427	−341	−1489	−356	−15.6	−3.7
$HCl{\cdot}200H_2O$	−1739	−416	−1822	−436	−20.5	−4.9
$HCl{\cdot}400H_2O$	−1942	−464	−2041	−488	−24.5	−5.9
$HCl{\cdot}800H_2O$	−2080	−497	−2185	−523	−26.3	−6.3
$HCl{\cdot}\infty H_2O$	....	[−590]	....	[−620]	....	...

The values for heats of dilution here presented are similar to those found by the earlier method of Richards and Rowe,[2] although not identical. The differences resulting from the newer method are due primarily to its greater accuracy and also to the use of more dilute solutions, for it is difficult to handle concentrated solutions such as were used in the earlier work. There are few other values in the literature which can be compared, since Thomsen[7] covered the range from $HCl{\cdot}2H_2O$ to $HCl{\cdot}300H_2O$ and Wrewsky and Sawaritzky[8] almost the same range. If the heat evolved

---

[6] The final temperature in these experiments was known within ±0.015°, as discussed in ref. 3 b, p. 712.

[7] Thornsen, "Thermochemische Untersuchungen," Leipzig, **1883**, Vol. III, p. 72.

[8] Wrewsky and Sawaritzky, *Z. Physik Chem.*, **112**, 90 (1924). See also Tucker, *Trans. Roy. Soc. London*, **215A**, 319 (1915).

is plotted against concentration, a smooth curve is obtained, which cannot be easily extrapolated to zero concentration since the curve approaches the axis very obliquely. This shows that thermo-neutrality is reached only with exceedingly dilute solutions.

On the other hand, extrapolation of the curve for specific heats plotted against concentration is more certain and yields the value of 1.000 at zero concentration. Table III compares the values for specific heats determined by different methods.

TABLE III

SPECIFIC HEATS OF HYDROCHLORIC ACID SOLUTIONS (REFERRED TO WATER AT THE SAME TEMPERATURE)

$HCl + nH_2O$	Richards, Mair and Hall 18°C. Direct	Richards, Mair and Hall Indirect	Richards and Rowe[a] 18°	Thomsen[b]	Marignac[c] 20–24°	Wrewsky[d] 20.5°
$25H_2O$	0.8766	....	0.8776	[0.876][e]	0.8787	[0.875]
$50H_2O$	.9337	0.9333	.9334	.932	.9336	.932
$100H_2O$	.9651	.9653	.9636	.964	.9650	.964
$200H_2O$	....	.9821	.9812	.979	.9835	[.981]

[a] Ref. 3a. See also Richards and Rowe, Proc. *Am. Acad.*, 49, 194 (1913).

[b] "Thermochemischen Untersuchungen," Vol. I, p. 38.

[c] "Oeuvres Complets," Vol. II, p. 624.

[d] Wrewsky and Kaigorodorff, *Z. physik.* Chem., 112, 83 (1924).

[e] Bracketed values were obtained by our interpolations.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

1. Specific heats of solutions of hydrochloric acid with 25, 50 and 100 moles of water per mole of acid were measured directly by the twin calorimeter method at 18°.

2. Heats of dilution of hydrochloric acid solutions were measured over the range $HCl \cdot 25H_2O$ to $HCl \cdot 800H_2O$ at 16 and 20°.

3. By the use of the Person-Kirchhoff relation the specific heats of the dilute solutions were calculated.

BRYN MAWR, PENNSYLVANIA
ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

FURTHER STUDIES ON THE THERMOCHEMICAL BEHAVIOR OF SODIUM HYDROXIDE SOLUTIONS[1]

BY THEODORE W. RICHARDS AND LAWRENCE P. HALL

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

Scope of Work

This paper contains an account of the investigation of the thermal behavior of sodium hydroxide solutions with a study of the heats of dilution of solutions more concentrated than $NaOH \cdot 25H_2O$. From these results the specific heats of the more concentrated solutions have been calculated. Further data were obtained to confirm the short extrapolation necessary to correct the heat of dilution of $NaOH \cdot 25.31H_2O$ and $NaOH \cdot 50.38H_2O$ to integral values.[2] Also the maximum of the curve for heats of dilution with decreasing concentration was determined at 20°.

In the latter part of this paper are collected the thermal data, dealing with sodium hydroxide solutions, which have been found in this Laboratory during the past twenty years. These data have been recalculated, whenever necessary, using the more accurate values for specific heats which have been published recently.[3]

Apparatus and Methods of Procedure

Since approximate results were desired as quickly as possible, an attempt was made to use a simple calorimeter consisting of a 500-cc. Dewar flask with glass stirrer, Beckmann thermometer, glass pipet (for delivering water) and cover. The pipet, bent into a compact U-shape (after the idea of Sugden),[4] was immersed in the hydroxide solution in the vacuum flask in order to keep all parts of the system at the same temperature. After measurement of the fore drift, the water in the pipet was blown by an aspirator bulb into the solution and the temperature change noted.

By this method it was evident that at about a dilution of $NaOH \cdot 17.5H_2O$ there was no measurable heat change upon the addition of small amounts of water. However. too much irregularity existed in this method to yield trustworthy results. Unless the solution inside the Dewar flask was at the same temperature as that of the room, there was always an important temperature drift. The large amount of glass permitted a large and uncertain heat interchange between the room and the solution. Thermal equilibrium within the Dewar was established very slowly. Added to these difficulties was the large and almost indeterminable heat capacity of the Dewar flask.

Accordingly, the Dewar flask calorimeter was abandoned and a simple adiabatic one, very similar to that used by Richards and Rowe,[5] was found to be more satisfactory in every respect.

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author.

[2] *Cf.* Richards and Gucker, THIS JOURNAL, 51,712 (1929).

[3] (a) Richards and Gucker, *ibid.*, 47, 1876 (1925); (b) Richards and Hall, *ibid.*, 51,707 (1929).

[4] Cf. Perman and Lovett, *Trans. Faraday Soc.*, 22, 10 (1926).

[5] Richards and Rowe, THIS JOURNAL, 42,1621 (1920).

The mercury thermometers (made especially for thermochemical work at 16 to 20°) were carefully standardized by comparison with a calibrated platinum resistance thermometer. Since the apparatus was not perfect, it was necessary to apply a small temperature correction for the drift which was measured both before and after each dilution experiment.

The solutions used in all these dilutions were made from recrystallized "c. p." sodium hydroxide. They contained a few tenths of 1% of carbonate, which would decrease the heat evolved on dilution, but the effect was beyond the accuracy of the method as performed with mercury thermometers. It was found, as would be expected, that a trace of carbonate although present in small varying amounts did not change the value of the temperature coefficients.

The following table summarizes the heats of dilution (corrected to exactly 16 and 20") and their temperature coefficients, expressed in calories, for the range of concentrations studied.

TABLE I

HEATS OF DILUTION (IN CALORIES)

Original soln.	Product of dilution	AH at 20°	AH at 16°	ΔC_p
$NaOH\cdot 10.0H_2O$	$NaOH\cdot 17.5H_2O$	**−93**	−60	− 8.2
$NaOH\cdot 10.0H_2O$	$NaOH\cdot 17.87H_2O$	−92	−59	− 8.2
$NaOH\cdot 17.87H_2O$	$NaOH\cdot 25.00H_2O$	+39	+60	− 5.3
$NaOH\cdot 10.0H_2O$	$NaOH\cdot 25.00H_2O$	−51	+ 4	−13.8
$NaOH\cdot 25.00H_2O$	$NaOH\cdot 26.00H_2O$	+ 5.4	+ 7	....

The value found for the change from $NaOH\cdot 25H_2O$ to $NaOH\cdot 26H_2O$ agrees with the value found by interpolation of the curve for heats of dilution which was used in the publication of this series by Richards and Gucker.[2] This corroboration is important because at a greater concentration than $NaOH\cdot 25H_2O$ the curve suddenly changes its course. Thomsen stated[6] that the change from heat evolved to heat absorbed occurred at about $NaOH\cdot 20H_2O$.

This change in the curve was studied by diluting a solution corresponding to the composition of $NaOH\cdot 10H_2O$ to many stages of dilution ($NaOH\cdot$-$11H_2O$ to $25H_2O$). The values thus obtained for 20" are presented in the small inset of Fig. 1.

This graph depicts the result of the different influences involved in dilution. It is also clear that if a solution of $NaOH\cdot 10H_2O$ were diluted to about $NaOH\cdot 35H_2O$ there would be no heat change. The ordinates thus form a series of "isothermal lines" up to $NaOH\cdot 200H_2O$.

Specific Heat of Concentrated Solutions.—From the temperature coefficients for the above heats of dilution the specific heats of the concentrated solutions can be calculated by the Person–Kirchhoff Law, using the specific heat of $NaOH\cdot 25H_2O$ as the basis.

In a similar way the specific heat of $NaOH\cdot 17.87H_2O$ can be calculated from the temperature coefficient of the dilution $NaOH\cdot 17.87H_2O$ to $NaOH\cdot$-

---

[6] Thomsen, "Thermochemische Untersuchungen," Leipzig, 1883, Vol. III, p. **83.**

Table II

Heat Capacities and Specific Heats of $NaOH \cdot 10H_2O$

Temperature, °C.	16	18	20
Heat capacity, mayers	3.630	3.619	3.641
Specific heat	0.865	0.868	0.871

$25.00H_2O$ as 0.8962 at 18°. If the value found for the specific heat of $NaOH \cdot 10H_2O$ is used as a basis in the dilution of $NaOH \cdot 10.00H_2O$ to $NaOH \cdot 17.87H_2O$, the specific heat value 0.8966 is obtained. These values agree well with that interpolated from the graph for specific heats at 18° plotted against dilution, 0.8965.

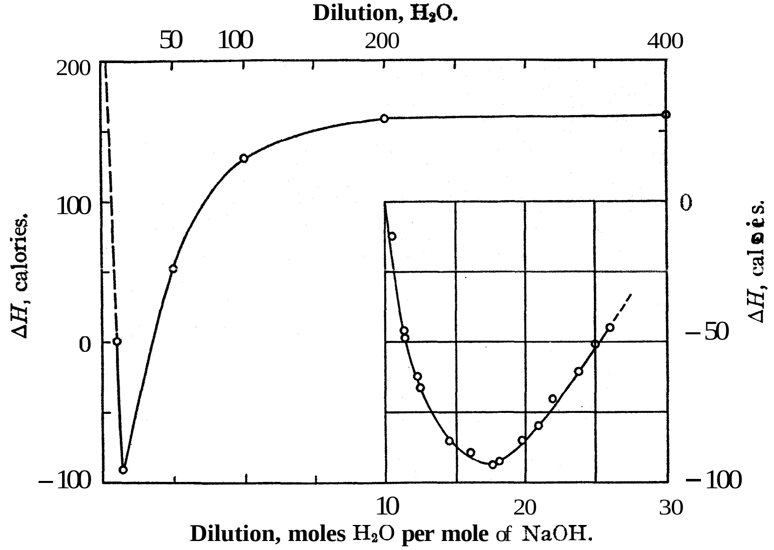


Fig. 1.

Recalculation of Earlier Data.—As was pointed out in a note in the article by Richards and Hall,[3b] the value for the specific heat of $NaOH \cdot 10H_2O$, 0.855, which was used by Richards and Rowe[7] as the basis of calculation, was too low. The recent accurate determination for the specific heat of sodium hydroxide solutions permits the recalculation of the heats of dilution and specific heats published in 1921. These recalculations are summarized in Tables III and IV.

For comparison with the results of Richards and Gucker[2] these values are calculated for the dilution of an initial solution of $NaOH \cdot 25H_2O$ in Table IV.

The good agreement between the recalculated values of Richards and Rowe and those recently published by Richards and Gucker is of particular importance as the stages of dilution in the two researches were quite dif-

---

[7] Richards and Rowe, This Journal, 43,770 (1921).

TABLE III

HEATS OF DILUTION OF SODIUM HYDROXIDE

From the data of Richards and Rowe, THIS JOURNAL, 43, 779 (1921).

Factors	Product	$-\Delta H_{16°}$, Joules	$-\Delta H_{16°}$, Cal.	$-\Delta H_{20°}$, Joules	$-\Delta H_{20°}$, Cal.	$-\Delta C_p$, Mayers	$-\Delta C_p$, Cal.
$NaOH \cdot 10H_2O + 15H_2O$	$NaOH \cdot 25H_2O$	+ 6	+ 1.4	+237	+ 56.7	57.8	13.8
$NaOH \cdot 10H_2O + 40H_2O$	$NaOH \cdot 50H_2O$	− 608	−143	−228	− 54.8	95	22.7
$NaOH \cdot 10H_2O + 90H_2O$	$NaOH \cdot 100H_2O$	− 999	−239	−532	−127	117	27.9
$NaOH \cdot 10H_2O + 190H_2O$	$NaOH \cdot 200H_2O$	−1204	−288	−652	−156	138	33
$NaOH \cdot 10H_2O + 390H_2O$	$NaOH \cdot 400H_2O$	−1242	−297	−674	−161	142	34

TABLE IV

COMPARISON OF HEATS OF DILUTION IN 20° CALORIES

Factors	Products	R. and R. $-\Delta H_{16°}$	R. and R. $-\Delta H_{20°}$	R. and G. $-\Delta H_{16°}$	R. and G. $-\Delta H_{20°}$
$NaOH \cdot 25H_2O + 25H_2O$	$NaOH \cdot 50H_2O$	−147	−111	−141	−105
$NaOH \cdot 25H_2O + 75H_2O$	$NaOH \cdot 100H_2O$	−240	−184	−240	−184
$NaOH \cdot 25H_2O + 175H_2O$	$NaOH \cdot 200H_2O$	−289	−213	−286	−213
$NaOH \cdot 25H_2O + 375H_2O$	$NaOH \cdot 400H_2O$	−299	−218	−298	−216
$NaOH \cdot 25H_2O + \infty$	....	...	...	−257	−163

ferent and as the methods were also sufficiently diverse to provide an excellent independent check.

Comparison of Specific Heat Values.—The recalculated heats of dilution make possible comparisons of the specific heat values determined by the two different methods of dilution, by direct measurement, and by other methods of experimentation.

TABLE V

SPECIFIC HEATS OF SODIUM HYDROXIDE SOLUTIONS AT 18° REFERRED TO WATER AT THE SAME TEMPERATURE

Solution	Richards and Hall, by direct detn.	Richards and Gucker, from heats of dilution	Richards and Rowe, from heats of dilution	Thomsen, directly	Others by various methods
$NaOH \cdot 10H_2O$	[0.8682][a]	.....	0.8680	(0.858)[b]	....
$NaOH \cdot 17.87H_2O$	[.896][a]	.....	....	(.888)[b]	....
$NaOH \cdot 25H_2O$	.91272	(0.91272)	(0.9127)	(.908)[b]	....
$NaOH \cdot 50H_2O$	.946	.94654	.9450	.942	....
$NaOH \cdot 100H_2O$	.96904	.96906	.9691	.968	0.9664[c]
$NaOH \cdot 200H_2O$	.....	.98319	.9830	.983	.9827[c]
$NaOH \cdot 400H_2O$	.....	.99122	.9913	...	....

[a] Calculated by the Person-Kirchhoff law from heat of dilution.

[b] By interpolation.

[c] Richards and Rowe, *Proc.* Am. *Acad.*, 49, 178 (1913). The error for the value 0.9664 is unexpectedly and inexplicably large. Its cause is not apparent.

It is interesting to note in connection with these comparisons that in the cases of solutions of other substances other experimenters have more recently obtained values consistent with those found by Richards and Rowe. Maass and others[8] have found by an entirely different method essentially identical values for the heat of dilution of sodium chloride.

---

[8] Lipsett, Johnson and Maass, THIS JOURNAL, 49, 925, 1940 (1927).

Lange,[9] working with others, has found confirming values for a number of salts by yet another method. The objection made by Lange[10] to the method of calculation used by Richards and Rowe, has since been courteously withdrawn.[11]

Recalculation of Heats of Neutralization.—The newer values for heats of dilution and specific heat make possible a still more accurate calculation of the heat of neutralization when sodium hydroxide solutions react with strong acids.[12] These new values improve considerably the extrapolation to infinite dilution for the curves plotted for heat of neutralization against dilution.[13]

TABLE VI

HEAT OR NEUTRALIZATION OF $NaOH \cdot 100H_2O$[a]

	18° Cal.	20° Cal.	Kj.
$HCl \cdot 100H_2O$	13,919	13,924	58.21
$HBr \cdot 100H_2O$	13,851	13,856	57.93
$HI \cdot 100H_2O$	13,792	13,797	57.68
$HNO_3 \cdot 100H_2O$	13,846	13,851	57.90

[a] This table replaces part of Table IV, THIS JOURNAL, 44, 699 (1922).

TABLE VII

HEATS OR NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN 20° CALORIES (TEMP., 20°)[a]

Moles H_2O	In factors	25+25	50+50	100+100	200+200	400+400	∞
	In products	51	101	201	401	801	∞
Reaction	NaOH+HCl	14,260	14,026	13,924	13,854	13,794	13,640
	$NaOH+HNO_3$	14,034	13,902	13,851	13,804	13,769	13,640

[a] This table replaces part of the table on p. 702, THIS JOURNAL, 44, (1922).

The values in Table VII for the heat of neutralization at infinite dilution were obtained by graphical extrapolation of the neutralization curves. Another method of finding this value is extrapolation of the heats of dilution of the factors and products to zero concentration and algebraic summation of these values. This may be done with least uncertainty in the case of the neutralization of hydrochloric acid. The dilution of sodium hydroxide has recently been discussed.[2] New values for the heat of dilution of hydrochloric acid recently determined in this Laboratory[14] indicate the evolution of 266 calories on dilution from $HCl \cdot 100H_2O$ to $HCl \cdot \infty H_2O$ at 20°. In order to obtain an extrapolated value for sodium chloride the heat of dilution measured by Richards and Rowe has[15] been combined

---

[9] (a) Lange, Z. *physik. Chem.*, 116, 337 (1925); (b) Wust and Lange, *ibid.*, 116, 162 (1925); (c) Lange and Durr, *ibid.*, 118, 129 (1925); (d) 121,361 (1926).

[10] Ref. 9 b, p. 189.

[11] Lange, Z. *physik. Chem.*, 117, 336 (1925).

[12] Richards and Rowe, THIS JOURNAL, 44, 684 (1922).

[13] *Cf.* ref. 12, p. 703.

[14] Richards, Mair and Hall, THIS JOURNAL, 51, 727 (1929).

[15] Richards and Rowe, *ibid.*, 43, 779 (1921).

with values found by Lipsett, Johnson and Maass[8] and also with those of Lange and Messner[16] at still smaller concentrations. The resulting curve is a regular one with an inflection at about $NaCl\cdot500H_2O$; at lower concentrations than this a small amount of heat is evolved. Using these values for the factors and products, the following thermochemical equations are obtained.

$NaOH\cdot100H_2O + HCl\cdot100H_2O$	=	$NaCl\cdot201H_2O$	13,924 Cal.
$NaCl\cdot201H_2O + (\infty - 201)H_2O$	=	$NaCl\cdot\infty H_2O$	15 Cal.
$HCl\cdot\infty H_2O$	=	$HCl\cdot100H_2O + (w - 100)H_2O$	−266 Cal.
$NaOH\cdot\infty H_2O$	=	$NaOH\cdot100H_2O + (\infty - 100)H_2O$	−20 Cal.
			13,653 Cal.

The agreement with graphical extrapolation is as good as could be hoped, with due consideration for the difficulties and uncertainties of extrapolations.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

1. The heat of dilution of $NaOH\cdot10H_2O$ has been measured at 16 and 20°. The change from heat evolved to heat absorbed was found to be at $NaOH\cdot17.5H_2O$ at 20°.
2. The specific heats of more concentrated solutions were calculated by the Person–Kirchhoff Law to be 0.868 at 18° for a solution of $NaOH\cdot10H_2O$, and 0.896 at 18° for $NaOH\cdot17.87H_2O$.
3. Earlier work with sodium hydroxide solutions on heats of dilution, specific heats and heats of neutralization has been recalculated and compared with recent researches.
4. The heat of neutralization at 20° of hydrochloric acid and sodium hydroxide is calculated to be 13.65 Cal. at infinite dilution.

ST. LOUIS MISSOURI

---

[16] Lange and Messner, *Naturwissenschaften*, 15, 521 (1927).

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE HEAT OF NEUTRALIZATION OF ACETIC ACID[1]

BY THEODORE W. RICHARDS AND BEVERIDGE J. MAIR

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

Introduction

The importance of an accurate determination of the heat of neutralization of acetic acid and its significance in calculating the heat of formation of water from its ions has been emphasized in a recent paper by Richards and Gucker.[2] In that investigation data were obtained from which the heat of neutralization at various concentrations could be calculated provided the heat of neutralization at any one concentration was known. The data hitherto available for the heat of neutralization of acetic acid were inadequate[3] to accomplish this with *a* degree of accuracy comparable to that of strong acids and bases previously investigated by Richards and Rowe,[4] for which recalculated values have been presented in a paper of this series.[5] In this paper are presented accurate data for the heat of neutralization of acetic acid and its change with concentration. From these data, together with those of strong acids and bases, a more probable value for the heat of formation of water from its ions is obtained.

Method and Apparatus

The apparatus was that used by Richards and Gucker for the determination of heats of dilution, modified slightly to make it suitable for the larger temperature changes involved.

The small bottom valve holes (designated a,b, by Richards and Gucker) were enlarged to a diameter of 2.5 mm., while the diameter of the large central valve (designated as c) was reduced to 6 mm. Platinum baffles were soldered over the small valve holes, a,b, in order to deflect the solution from the bottom of the calorimeter into the paths of the stirrers in the annular space.

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] Richards and Gucker, THIS JOURNAL, 51, 712 (1929).

[3] Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, Vol. I, p. 271, gives the value 13.40 Cal. for the heat of neutralization of $HC_2H_3O_2{\cdot}200H_2O$ at 20°, and Mathews and Germann, J. Phys. Chem., 15, 75 (1911), give the value 13.23 Cal. for *N*/4 acetic acid. These values are probably low. Thomsen's results for strong acids are about 2.5% lower than those of Richards and Rowe, while Mathews and Germann used unstandardized thermometers and a Dewar flask as a calorimeter. They disclaimed high accuracy.

[4] Richards and Rowe, THIS JOURNAL, 44, 684 (1922).

[5] Richards and Hall, *ibid.*, 51, 731 (1929).

The experiment was performed by opening the two small bottom valves (a,b), the central valve *c* about thirty minutes later when mixing was about three-quarters complete and finally five minutes later the side valves. By this procedure the presence of a hot layer on top, with the deleterious effect produced by distillation of water from the solution to the submarine lid was avoided. The temperature difference between the outer bath and calorimeter was well within 0.01° during most of the experiment but rose to 0.04° for about thirty seconds after the central valve was opened. This approach to true adiabacity with the air gap in question was adequate to obtain an accuracy of 0.001° in the measurement of temperature change. Corrections for the temperature drift were applied and the temperature rise was calculated from the resistance change as described by Richards and Gucker.

The heat capacity of the apparatus (76.4 mayers) was calculated from the sum of the heat capacities of its constituent parts in the manner described in the previous publication.[2]

Preparation and Analyses of Solutions

The sodium hydroxide solution was purified and protected from carbon dioxide in essentially the same manner as that previously employed in this Laboratory.[4,6] Titration with pure standard hydrochloric acid, using weight burets, showed its concentration to be $NaOH\cdot 100.99H_2O$. The acetic acid solution was prepared from crystallized glacial acetic acid and by comparison with standard sodium hydroxide proved to be of the concentration $HC_2H_3O_2\cdot 100.36H_2O$.

TABLE I

HEAT OF NEUTRALIZATION OF ACETIC ACID WITH SODIUM HYDROXIDE[a]

$HC_2H_3O_2\cdot 100.36H_2O + NaOH\cdot 100.99H_2O$

Weight, g.	Heat cap./g. mayers	Total heat cap. incl. cal. (mayers)	AT	Final T	Δh, Joules	ΔH, Joules
610.63A	4.1338	.....	3.627	19.98	−18413	−56331
610.78B	4.0537	5076.54	3.627	20.02	−18413	−56331
.....	....	.....	3.625	20.06	−18403	−56300
.....	....	.....	3.627	20.06	−18413	−56331

Average (AH) corrected to 20.00° = −56324

[a] A slight excess of sodium hydroxide was used throughout to avoid as far as possible errors which result from the presence of sodium carbonate.

Ah refers to the heat absorbed by the quantity used in the actual experiment, while ΔH refers to molal quantities. A and B stand for weights of solutions of acid and base, respectively; the rest of the table is self-explanatory.

The specific heats of the solutions were computed from the values at 18° given by Richards and Gucker[2] for solutions containing exactly 100

---

[6] Richards and Gucker, THIS JOURNAL, 47, 1882 (1925).

moles of water per mole of acid or base by correction for the additional water they contained, with the aid of the Person-Kirchhoff equation.

The heats of neutralization of acetic acid with changing concentration are shown in Table II. The results were calculated from the heats of dilution of factors and products[4] with the aid of the well-known thermochemical equations.

TABLE II

HEAT OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN JOULES (20°)

	Moles of H_2O				
In factors	50+50	100+100	200+200	400+400	800+800
In products	101	201	401	801	1601
$HC_2H_3O_2$ + NaOH	55975	56324	56539	56659	56714

The values given in Table II are depicted graphically in Fig. 1, together with the corresponding values[5] for hydrochloric and nitric acids. Independent extrapolations of these curves to infinite dilution yield values ranging from 56.78 to 57.40 kj. Since the reaction at infinite dilution becomes merely $H^+ + OH^- = H_2O$, these curves should approach a common value. Consequently, extrapolation to a point of convergence probably gives a more trustworthy value than the average of the independent extrapolations. Since the curves approach the zero concentration axis from different angles, extrapolation to a point of convergence is less uncertain than was the case with strong acids alone, in which all approached the zero concentration axis from the same direction. A graphical extrapolation to the most probable point of convergence yields the value 57.07 kj. or 13.65 Cal. for the heat of neutralization at infinite dilution.

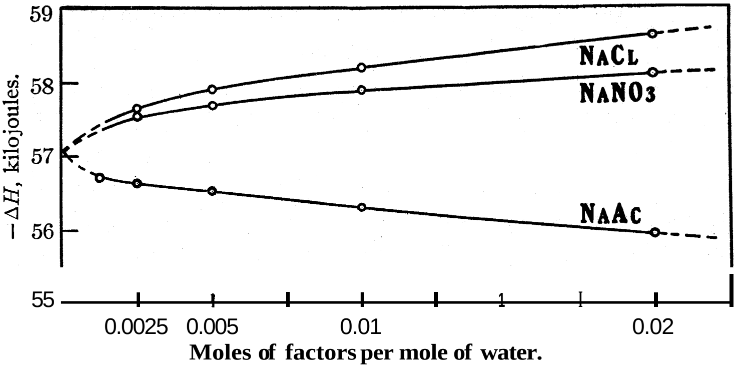


Fig. 1

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

The heat of neutralization of acetic acid and sodium hydroxide was found to be 54,324 joules at 20° at concentrations of $HC_2H_3O_2 \cdot 100H_2O$ and $NaOH \cdot 100H_2O$. The heat of neutralization at other concentrations is calculated with the aid of thermochemical data presented in previous publications. By extrapolation, upward for acetic acid and downward for strong acids, the heat of reaction $H^+ + OH^- = H_2O$ was found to be 57.07 kj. or 13.65 Cal. at 20°.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A STUDY OF THE THERMOCHEMICAL BEHAVIOR OF WEAK ELECTROLYTES[1]

BY THEODORE W. RICHARDS AND BEVERIDGE J. MAIR

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

Introduction

Within the past few years the thermochemical behavior of aqueous solutions of many strong electrolytes has been investigated in this Laboratory.[2] The present investigation is a continuation of that work, particularly with weak electrolytes. Heats of dilution at 16 and 20° of aqueous solutions of citric acid, sodium citrate and the acid citrates were measured and from these values the heat capacities of the resulting solutions calculated by means of the Person–Kirchhoff equation.[2d] The heats of neutralization of citric acid and its acid salts were also measured and from the heats of dilution of factors and products the heat of neutralization at various concentrations was calculated. The significance of such measurements in connection with solution theories needs no explanation. The heats of dilution and resulting heat capacities will be considered first.

Apparatus and Method

The apparatus and experimental procedure have been adequately described elsewhere.[2d,e] The large absorption of heat on dilution of the citrates, however, necessitated one minor modification. A reservoir for ice and water, supported four feet above the apparatus, was connected to a circular rose in the outer bath. The rose, made out of glass tubing with small apertures three inches apart, encircled the "submarine" and

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] (a) Richards and Rowe, THIS JOURNAL, 42, 1622 (1920); (b) 43, 771 (1921); (c) 44, 684 (1922); (d) Richards and Gucker, *ibid.*, 51, 712 (1929); (e) Richards, Mair and Hall, ibid., 51, 727 (1929).

permitted the addition of ice water to take place throughout the bath rather than at any one spot. This, together with the efficient stirrer already in the bath, made it possible to add water rapidly without appreciable thermal inhomogeneity. Since the calorimeter system was identical with that used by Richards, Mair and Hall[2e] its heat capacity was taken as 76.4 mayers, the value previously obtained by them from the heat capacity of its constituent parts.

Purification and Analyses of Solutions Used in the Dilution Experiments

Sodium Citrate Solution.—Sodium citrate, the best obtainable, was further purified by a single crystallization with centrifuging, dried in the oven at 100° and dissolved to make a solution approximately $Na_3C_6H_5O_7\cdot 50H_2O$. The solution was then analyzed by digesting a weighed quantity with sulfuric acid in a long-necked quartz flask of about 100 cc. capacity. The digestion mixture, when clear, was transferred to a weighed platinum crucible and evaporated to dryness on a ring burner. It was fused to constant weight and weighed as Na_2SO_4. The residues were examined for SiO_2, tested for excess SO_3 with methyl orange, and showed no signs of either. Four analyses showed the solution to be of the concentration $Na_3C_6H_5O_7\cdot 49.35 \pm 0.01H_2O$.

Citric Acid Solution.—The best obtainable citric acid was further purified by a single crystallization with centrifuging and dissolved to make a solution of approximately the desired concentration. Two analyses with carbonate-free sodium hydroxide, using phenolphthalein as an indicator, showed the solution to be of the concentration $H_3C_6H_5O_7\cdot 25.07H_2O$. 0.07 g. of thymol was added to three liters of solution. This quantity, insufficient to alter the heat capacity of the solution, adequately prevented the formation of mold.

Monosodium Dihydrogen Citrate and Disodium Monohydrogen Citrate Solutions.—These solutions were made up determinate to the concentrations $NaH_2C_6H_5O_7\cdot 50H_2O$ and $Na_2HC_6H_5O_7\cdot 50H_2O$, using the citric acid and sodium citrate solutions which had been previously analyzed.

Reference to the papers previously mentioned will show how the results were calculated. The rise in temperature, *At*, was the average of two or more experiments agreeing within 0.0003". In a few cases, where there was a larger discrepancy caused by some temporary minor difficulty, a greater number of experiments were performed so that the average deviation from the mean was in no case greater than ±0.0004°. The heat capacities of the most concentrated solutions used in the calculation of the first stage of the heat of dilution were the instantaneous values at 16 and 20°, directly determined by Richards and Gucker,[3] while for the subsequent dilutions the heat capacity at 18° (calculated by means of the Person–Kirchhoff equation) was used to compute the heat of dilution at both 16 and 20°. This approximation was adequate for the accuracy desired.

The experimental data, corrected to integral stages where necessary, are summarized in the following tables.

The values given in Table II for the heats of dilution are depicted graphically in Fig. 1, in which ordinates represent heats of dilution and abscissas

---

[3] Richards and Gucker, THIS JOURNAL, 47, 1876 (1925).

TABLE I

HEAT CAPACITIES PER GRAM AT 18° IN MAYERS

	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$	$1600H_2O$
$H_3C_6H_5O_7$	3.7326	3.9313	4.0487	4.1134	4.1470	....
$NaH_2C_6H_5O_7$	3.6700	3.8778	4.0124	4.0915	4.1348	4 1579
$Na_2HC_6H_5O_7$	3.5921	3.8187	3.9734	4.0683	4.1222	4.1512
$Na_3C_6H_5O_7$	3.4987	3.7443	3.9241	4.0388	4.1057	....

TABLE II

HEATS OF DILUTION AND THEIR TEMPERATURE COEFFICIENTS

	Total moles of water in final solution					
	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$	$1600H_2O$
			$H_3C_6H_5O_7{\cdot}25H_2O$			
AH at 16°, joules	511	900	1178	1393	1605	1838
ΔH at 20°	465	818	1072	1282	1475	1714
AC„ mayers	11.5	20.5	26.5	27.8	32.5	31.0
			$NaH_2C_6H_5O_7{\cdot}50H_2O$			
AH at 16"		2066	3449	4256	4688	....
AH at 20°		1896	3138	3847	4210	4380
ΔC_p		42.5	77.8	102.3	119.5	....
			$Na_2HC_6H_5O_7{\cdot}50H_2O$			
AH at 16"		3129	5378	6721	7405	7711
AH at 20°		2851	4857	6019	6584	6812
ΔC_p		69.5	130.2	175.5	205.3	224.5
			$Na_3C_6H_5O_7{\cdot}50H_2O$			
ΔH at 16°		2948	5226	6595	7234	7400
ΔH at 20°		2509	4409	5484	5924	[6180]
ΔC_p		109.8	204.2	277.8	327.5	....

fractions of a mole of salt per mole of water. It is worthy of note that there is no regularity between the heats of dilution of these substances due to the replacement of hydrogen by sodium.

In Table III the heats of dilution, AH, of acetic and citric acids are compared with their degrees of ionization.[4] The first two rows represent the concentration and corresponding degree of dissociation, while the third and fourth rows give the change in ionization and corresponding heat of dilution between the concentrations given in the first row.

---

[4] The only one of the substances investigated in this research on which data necessary for the calculation of the degree of ionization are available is citric acid. Acetic acid, for which accurate data for the heats of dilution have been published in a recent paper of this series (Richards and Gucker, THIS JOURNAL, 51,712 (1929), is the classical example given for the Ostwald dilution law and is consequently particularly suitable for this comparison. The degree of ionization was calculated by the approximate formula $\alpha^2 = K/c$, where α = fraction ionized, c = concentration in moles per liter and K is the equilibrium constant. The dissociation constants used for acetic and citric acids were 1.8 X 10^{-5} and 0.082 $\times$ 10^{-5}, respectively (Creighton and Fink, "Electrochemistry," 1924, Vol. I, p. 309). Accuracy adequate for the present purpose was obtained by neglecting the dissociation of the secondary and tertiary hydrogens of citric acid.

Table III

Comparison of Heat of Dilution and Ionization

Acetic acid	$25H_2O$		$50H_2O$		$100H_2O$		$200H_2O$		$400H_2O$		$800H_2O$
$a \times 10^{-3}$	3.04		4.16		5.78		8.13		11.46		16.14
$\Delta a \times 10^{-4}$		11.2		16.2		23.5		33.3		46.8	
ΔH, joules		−296.6		−164.8		−83.7		−42		−22	
Citric acid	$25H_2O$		$50H_2O$		$100H_2O$		$200H_2O$		$400H_2O$		$800H_2O$
$a \times 10^{-4}$	7.25		9.46		12.76		17.69		24.6		34.5
$\Delta a \times 10^{-5}$		22.1		33.0		49.3		69.4		98.7	
ΔH, joules		464		353		254		210		193	

An examination of the third and fourth rows shows immediately that the heat change evolved does not parallel the increase in ionization, the heats of dilution decreasing while the change in degree of ionization increases. These results indicate that some other factor or factors must be largely responsible for the heat of dilution (in the range studied), although they do not preclude the possibility that there is a heat effect **due** to ionization masked by some larger effect. Other factors besides ioniza-

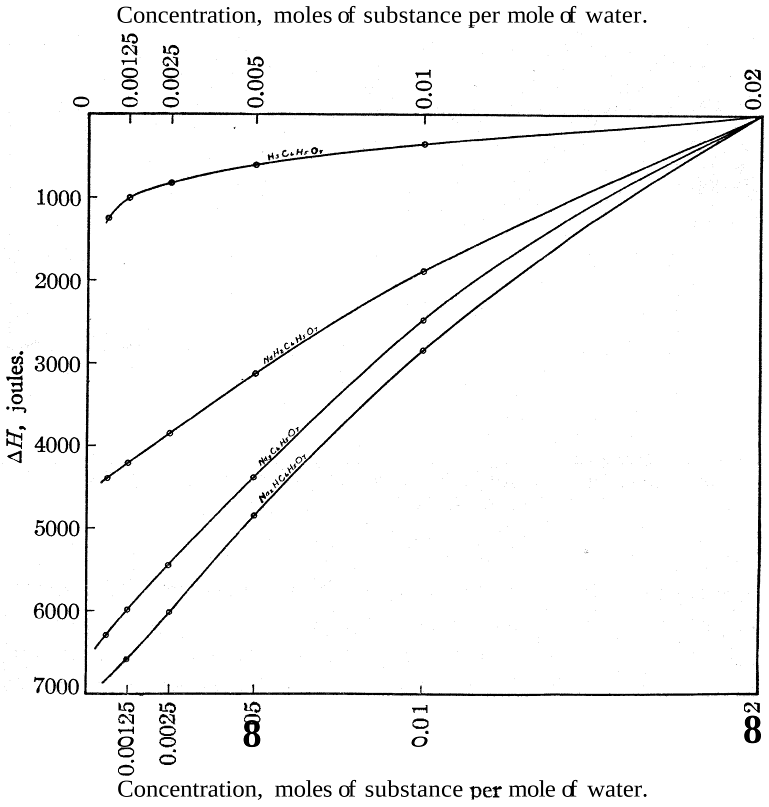
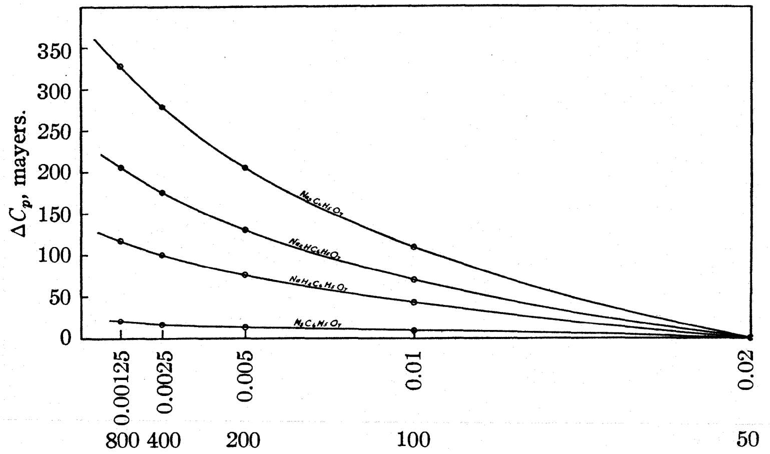


Fig. 1.—Heats of dilution.

tion responsible for the heat effect might be polymerization or depolymerization of solvent and solute molecules and solvation of molecules or ions of solute.

Another series of quantities worthy of consideration is loss of heat capacity on dilution. These values are depicted graphically in Fig. 2 in a manner identical with that employed for the heats of dilution. An examination of the curves shows that each hydrogen replaced by sodium in the citrates produces an increase in the loss of heat capacity which is almost regular. As was pointed out, no such regularity existed with the heat of dilution. This may be taken to indicate that loss of heat capacity is a function of fewer variables than heat of dilution. Richards and Rowe[2b] have pointed out that ionization should be accompanied by a decrease in heat capacity since the neutralization of strong acids and bases in which H^+ and OH^- are de-ionized is accompanied by an increase in heat capacity. It is interesting to see whether differences in degree of ionization can explain the regularity observed in the loss of heat capacity of the citrate solution. The strength of these substances as electrolytes increases from citric acid to sodium citrate and the percentage increase in ionization over the range investigated probably increases in the same order. Since this is the order in which the loss of heat capacity increases, it is apparent that the loss of heat capacity in these solutions depends to a large extent on the number of ions formed.



Concentration, (a) moles of substance per mole of water. (b) Moles of water per mole of substance.

Fig. 2.—Loss of heat capacity.

The total molal heat capacities are tabulated in Table IV.

These values (in the dilute solutions, at least) exhibit some regularity, heat capacity decreasing as hydrogen is replaced by sodium. This is

TABLE IV

MOLAL HEAT CAPACITIES AT 18° IN MAYERS

	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$
$H_3C_6H_5O_7$	4079.5	7837.7	15366	30433	60566
$NaH_2C_6H_5O_7$	4091.5	7816.3	15316	30361	60479
$Na_2HC_6H_5O_7$	4083.6	7781.1	15255	30278	60385
$Na_3C_6H_5O_7$	4054.4	7711.9	15152	30147	60234

exactly contrary to the behavior of strong inorganic acids, in which Richards and Rowe found the replacement of hydrogen by sodium to be accompanied by an increase in heat capacity. At infinite dilution it might be expected that the replacement of each hydrogen by sodium would produce the same change in heat capacity, since in such a condition the solution would be completely ionized and the difference in heat capacities would be simply the difference between the heat capacities of the hydrated sodium and hydrogen ions. The above solutions do not show a constant difference nor could it be expected that they would, since citric acid even in $800H_2O$ solutions is but slightly ionized. Some tendency toward a constant difference is noticeable as the solutions become dilute.

Heats **of Neutralization.**—The heat of neutralization of citric acid and its acid salts was determined with the same apparatus and in a manner identical to that previously employed to determine the heat of neutralization of acetic acid.[5]

The purification and analysis of the sodium hydroxide were performed with all the precautions previously described in publications from this Laboratory.[2c,6]

The citric acid was purified and analyzed in the same manner as in the dilution experiments. The acid salt solutions were made up determinate from standard sodium citrate (analyzed as described in the dilution experiments) and citric acid solutions.

By titration with standard sodium hydroxide a direct comparison of the solutions thus prepared was obtained. The results of the direct analyses and the determinate values agreed satisfactorily in all cases.

With disodium monohydrogen citrate a slight excess of base was used to eliminate as far as possible any uncertainty caused by traces of carbonate in the sodium hydroxide. Since this procedure was not possible with citric acid and monosodium dihydrogen citrate, exactly equivalent quantities were used.

The essential experimental data are recorded in Table V. *AT* is the average of at least five experiments which agreed within 0.003° in the cases of citric acid and disodium monohydrogen citrate. The results were not as concordant with monosodium dihydrogen citrate, in which case

---

[5] Richards and Mair, THIS JOURNAL, 51,737 (1929).

[6] Ref. 3, p. 1882.

the average deviation from the mean was 0.004". *Ah* refers to the heat absorbed by the quantities used in the actual experiment, while AH refers to molal quantities. A and B refer to acid and base, respectively.

TABLE V

HEATS OF NEUTRALIZATION OF CITRIC ACID AND ITS ACID SALTS

Weight, g.	Ht. cap. per g., mayers	Total heat cap. incl. Cal. (mayers)	AT, av.	Final T	*Ah* Joules	AH Joules
Citric Acid (Series I). $NaOH\cdot 100.99H_2O + H_3C_6H_5O_7\cdot 100.79H_2O$						
630.00A	3.9330	4918.9	3.400	19.95	–16726	–53310
583.42B	4.0537	Average at 20° = –53305				
(Series II). $NaOH\cdot 100.99H_2O + H_3C_6H_5O_7\cdot 100.00H_2O$						
630.00A	3.9313	4934.5	3.413	19.80	–16844	–53309
587.53B	4.0537	Average at 20.00° = –53291				
Monosodium Dihydrogen Citrate. $NaOH\cdot 99.75H_2O + NaH_2C_6H_5O_7\cdot 100H_2O$						
640.60A	38778	4925.7	3.428	19.88	–16884	–53136
583.73B	4.0523	Average at 20° = –53130				
Disodium Monohydrogen Citrate. $NaOH\cdot 99.75H_2O + Na_2HC_6H_5O_7\cdot 100H_2O$						
640.62A	3.8187	4875.2	3.524	20.05	–17180	–54664
580.60B	4.0523	Average at 20.00° = –54663				

The temperature coefficients of the heats of neutralization were calculated from the heat capacities of the factors and products with the aid of the Person–Kirchhoff equation and are given in the following table.

TABLE VI

TEMPERATURE COEFFICIENT OF HEAT OF NEUTRALIZATION

	Molal heat cap. of fac. at 18°, mayers	Total mayers, *K*	Molal heat cap. of prod. at 18°, mayers, *K*	Average $\frac{\Delta(\Delta H)}{\Delta T}$ or ΔC_p
$H_3C_6H_5O_7\cdot 100H_2O$	7837.7	15301.0	15391.0	+90.0
$NaOH\cdot 100H_2O$	7463.3			
$NaH_2C_6H_5O_7\cdot 100H_2O$	7816.3	15279.6	15329.9	+50.3
$NaOH\cdot 100H_2O$	7463.3			
$Na_2HC_6H_5O_7\cdot 100H_2O$	7781.1	15244.4	15226.7	–17.7
$NaOH\cdot 100H_2O$	7463.3			

The molal heat capacity of the product was obtained by adding to the molal heat capacity of the $200H_2O$ solution the heat capacity of one mole of H_2O and correcting this value for loss of heat capacity on dilution with the aid of curves for ΔC_p given in Fig. 2.

It is interesting to note that two of these acids show a much smaller increase in heat capacity on neutralization than the strong inorganic acids investigated by Richards and Rowe, while one of them actually shows a decrease in heat capacity. This is fully in accord with what has been noted previously with regard to loss of heat capacity and ionization. The degree of ionization of weak acids being less, the total decrease of ions in the solution on neutralization is less also, so that a smaller increase in heat capacity is to be expected. Even the behavior of $Na_2HC_6H_5O_7$ is not so very abnormal. The concentration of hydrogen ions from $Na_2HC_6H_5O_7\cdot 100H_2O$ is probably quite small, so that it is quite conceivable that there actually are more ions present in $Na_3C_6H_5O_7\cdot 200H_2O$ than in equivalent quantities of $NaOH\cdot 100H_2O$ and $Na_2HC_6H_5O_7\cdot 100H_2O$. Whether this is true is not of great significance since examples of a decrease in heat capacity may be expected in such border cases in which changes of solvation of molecules and polymerization of solvent mask the effect produced by increase in the number of ions formed.

The heats of neutralization of these acids with changing concentration are recorded in Table VII. The results were calculated from the heats of dilution of factors and products with the aid of the well-known thermochemical equations.

TABLE VII

HEAT OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN JOULES

(TEMPERATURE, 20°)

Moles of H_2O in factors	50 + 50	100 + 100	200 + 200	400 + 400	800 + 800
In products	101	201	401	801	1601
$H_3C_6H_5O_7$ + NaOH	53881	53298	52965	52825	52806
$H_2NaC_6H_5O_7$ + NaOH	52934	53130	53332	53489	53582
$HNa_2C_6H_5O_7$ + NaOH	53406	54663	55716	56441	56680

The values for the heat of neutralization of these acids are much smaller than those obtained by Richards and Rowe for strong inorganic acids. Furthermore, they do not approach the value 57.07 kj. to which these stronger acids tend at infinite dilution. These substances are, however, only slightly ionized even in the most dilute solutions investigated, so that it is probable that heat effects due to their ionization continue into solutions infinitely dilute.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

1. The heats of dilution of citric acid, the acid citrates and sodium citrate have been measured at 16 and 20° over the concentration range of 50 moles to 1600 moles of water per mole of substance.

2. The heat capacities over the same range have been calculated with the aid of the Person–Kirchhoff equation.

3. No relationship has been found to exist between the degree of ionization and heat of dilution. Hence some factor or factors other than ionization play a predominant part in the heat of dilution of these solutions.

4. The regularity in the decrease of heat capacity of these solutions has been explained as due to the number of ions formed.

5. The heat of neutralization of citric acid and the acid citrate has been measured. The values found are much less than for strong acids. The temperature coefficient of the heat of neutralization of these acids is decidedly smaller than for inorganic acids and, indeed, in one case, is of opposite sign. These results are discussed.

BRYN MAWR, PENNSYLVANIA

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

THE VAPOR PRESSURE AND VAPOR DENSITY OF INTENSIVELY DRIED AMMONIUM CHLORIDE[1]

BY WORTH H. RODEBUSH AND JOHN C. MICHALEK

RECEIVED OCTOBER 8, 1928 PUBLISHED MARCH 6, 1929

The anomalous behavior of intensively dried ammonium chloride was first reported in the literature by Baker,[2] who found that the vapor density as determined by a Victor Meyer method indicated no dissociation into ammonia and hydrogen chloride. Baker's work was repeated by Gutmann,[3] who obtained results indicating complete dissociation. Baker[4] again repeated his measurements and remained convinced that the vapor density of intensively dried ammonium corresponds to no dissociation. Two determinations of vapor density were made upon dried ammonium chloride by Johnson[5] with contradictory results. Smith, Eastlack and Scatchard[6] report that Smith and Lombard found no dissociation for dry ammonium chloride vapor but these results have not been published. Most investigators have found the vapor of moist ammonium chloride to be completely dissociated, but here again there is lack of complete agreement and Smith and Lombard[7] in an extensive investigation found only partial dissociation for undried ammonium halides.

---

[1] This manuscript was prepared for publication some months ago but publication has been delayed because of the appearance of a preliminary report by A. Smits [*Rec. trav. chim.*, **46**, 445 (1927)] of a similar series of experiments, with results differing from those here reported. A note was published by the authors [*Proc. Nat. Acad.*, **14**, 131 (1928)] commenting on the discrepancies between the two series of experiments. Since a detailed report of Smits' experiments has not appeared, it seemed advisable to submit the manuscript for publication as originally prepared. Meanwhile a paper has appeared by Braune and Knoke [*Z. physik. Chem.*, **135**, 49 (1928)] reporting measurements on undried ammonium chloride which are in substantial agreement with those described in this paper.

[2] Baker, *J. Chem. Soc.*, **65**, 611 (1894).

[3] Gutmann, *Ann.*, **299**, 267 (1898).

[4] Baker, *J. Chem. Soc.*, **73**, 422 (1898).

[5] Johnson, *Z. physik. Chem.*, **61**, 458 (1908).

[6] Smith, Eastlack and Scatchard, THIS JOURNAL, **41**, 1961 (1919).

[7] Smith and Lombard, *ibid.*, **37**, 48 (1915). These authors give references to previous determinations.

Several determinations[8] have been made upon the vapor pressure of undried ammonium chloride, of which the work of Smith and Calvert is probably the best. Johnson, however, made measurements on both dried and undried specimens of ammonium chloride. His measurements were made with a spiral glass manometer under conditions which did not ensure high accuracy, but they indicated that the vapor pressures of the dried and undried forms were identical. This last result has appeared to many as very surprising indeed and the theoretical implications have been discussed at some length by Abegg[9] and Wegscheider.[10]

If the vapor pressures of the dried and undried forms are the same and the vapor of the one is dissociated while the vapor of the other is not, we have a situation very difficult to explain, for there must exist an equilibrium between the dissociated and undissociated molecules in the vapor state and in turn between each of these and the solid. The removal of the last traces of moisture must be supposed to shift this equilibrium. The most probable way in which this could be imagined to come about would be for the removal of the last traces of moisture to increase the free energy of the solid and in addition prevent the establishment of the dissociation equilibrium. This is not necessarily a thermodynamic impossibility, since the removal of traces of moisttire might conceivably involve large energy changes, but it is certainly contrary to experience. Results so surprising as these cannot be accepted without ample experimental confirmation and it appeared to the authors that it would be worth while to redetermine the vapor pressures and vapor density of ammonium chloride in various stages of dryness.

Experimental

Method of Drying.—The term "intensively dried" used in this paper is, of course, relative. In his work on liquids, Baker[11] used materials which had been dried for several years. In the case of ammonium chloride, however, all authors who observed abnormal behavior have obtained this result after drying for a period of a few days to a few weeks. The following general procedure was used in the preparation of what we designate as "intensively dried" material.

The apparatus of pyrex glass was baked out for eight to ten hours at 400–500°. During this outgassing process it was connected to the drying pump system and the highest possible vacuum maintained. Attached to the apparatus by a tube which projected outside the furnace was a bulb containing the sample of ammonium chloride

---

[8] Smith and Menzies, THIS JOURNAL, 32, 1448 (1910); Smith and Calvert, *ibid.*, 36, 1363 (1914); Johnson, *Z. physik. Chem.*, 65, 38 (1909); Ramsay and Young, *Phil. Trans. Roy. Soc.*, 177, 71 (1886); Horstman, Ber., 2, 137 (1869).

[9] Abegg, *Z. physik. Chem.*, 61,455 (1908).

[10] Wegscheider, *Z. anorg. allgem. Chem.*, 103,207 (1918).

[11] Baker, J. *Chem. Soc.*, 121,2555 (1922).

which was to be introduced. When the apparatus was cool this sample was introduced by repeated sublimations until it was spread in a thin layer over the inside of the apparatus. A high vacuum was maintained during this process so that the salt as introduced was free from all but minute traces of moisture. The temperature of the apparatus was then raised to the highest point (60–70°) which could be maintained without driving the salt out of the apparatus and the pumping out process was continued for five to ten days. The pump and drying-tube system merit a detailed description. The apparatus containing the salt to be dried was connected to a mercury vapor diffusion pump of special design and high capacity. Beyond this pump was a drying tube containing phosphorus pentoxide which had been introduced by distillation in a current of oxygen. Beyond this drying tube was an ordinary diffusion pump, another phosphorus pentoxide tube and then a high-vacuum type of oil pump. Liquid-air traps were used whenever their use appeared advantageous. It must be recognized, however, that a liquid-air trap in a line has the same effect on the passage of water vapor as a very narrow constriction.

The "superpump" was designed by one of the authors to take care of a defect in the ordinary diffusion pump that has been pointed out by Molthan.[12]

In the ordinary type of diffusion pump the mercury is condensed against a cold surface and runs back into the reservoir whence it is reevaporated and goes around the circuit again. Any substance, e. g., water, which the pump is removing from the vessel to be evacuated will be to a slight extent dissolved in and adsorbed on the surface of the condensing drops of mercury. This establishes in the ascending column of mercury vapor a small but definite partial pressure of water vapor and the limit of exhaustion is reached when the partial pressure in the vessel to be evacuated has reached this value. The phosphorus pentoxide tube immediately beyond the pump would tend to overcome this difficulty but it was felt that the design of the pump could be materially improved and the model shown in Fig. 1 was devised. It is not possible to avoid the condensation against a cold surface but the drops of mercury flow down against a refluxing stream of hot mercury vapor, so that any volatile constituent should be distilled out before the mercury reaches the reservoir. For the construction of the difficult seal we are indebted to Dr. Phipps of this Laboratory. The pump functioned perfectly and showed a high capacity on test with a McLeod gage. No stopcocks or rubber connections were used between the apparatus containing the material to be dried and the diffusion pumps. The tube connecting the apparatus to the pump system was preheated thoroughly at the point where the final seal off was to be made. It is believed that drying under the above-described conditions of high vacuum and elevated temperature is far more rapid than with the ordinary technique that has been used by previous investigators.

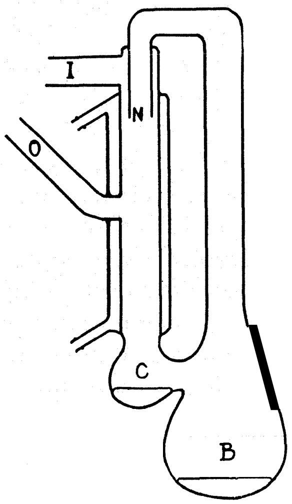


Fig. 1.

Materials.—The ammonium chloride used was either Mallinckrodt's or Kahlbaum's reagent quality. It did not give tests for other halogens and left no residue on sublimation. It was always introduced into the apparatus by repeating sublimation. Upon prolonged heating the ammonium chloride took on a yellowish tinge but there was no evidence of appreciable decomposition. The phosphorus pentoxide was Mallinckrodt's reagent quality. It was purified by distillation in a current of oxygen.

---

[12] Molthan, Z. *Physik*, 39, 1 (1926).

The distillation of phosphorus pentoxide in pyrex glass was always a troublesome operation.

The Vapor Pressure of Moist and Dry Ammonium Chloride.—By far the most satisfactory apparatus for measuring vapor pressures of substances like ammonium chloride is the glass diaphragm manometer. We are indebted to Professor Farrington Daniels for his experience in the construction of this gage and the apparatus shown in Fig. 2 embodies his latest ideas in its construction. The side tube A contains the ammonium chloride and is kept cool while the rest of the apparatus is being baked out. When the ammonium chloride is introduced into the main part of the apparatus the side tube A is sealed off. Connection is made with the drying pumps through the Tube G. When vapor pressure determinations are to be made the Tube G is sealed off under a high vacuum and the apparatus is introduced into a fused nitrate bath to the level shown at I. The details of the gage have been described by Professor Daniels. It is only necessary to note one point. The zero point of the gage changes with the temperature and (possibly) with the lapse of time, so that it must be rechecked after each determination. The tube G projects above the bath and may be cooled by a blast of air. When this is done the ammonium chloride sublimes out of the bulb and condenses in the tip of G, giving practically zero pressure in the apparatus. When a determination is to be made a heating coil is slipped over the end of the tube and the salt is driven back into the main part of the apparatus. The nitrate bath was provided with a thermo-regulator and while measurements were being taken the temperature was held constant to 0.02°. Temperatures were registered by means of thermocouples calibrated against fixed points recommended by the U. S. Bureau of Standards and temperature control of the bath was maintained by an automatic regulator which was actuated through a contact galvanometer by a thermocouple. The pressures on the outside of the diaphragm were measured by a mercury U-tube manometer. The vacuum above the mercury on the high side of this manometer was maintained by a mercury vapor pump. The heights of the mercury columns were measured with a cathetometer and repeated readings taken during a period of some hours usually checked to a few hundredths of a millimeter. The height of the mercury column was corrected to 0°. For the determinations on the moist salt the apparatus was sealed off from the pumps as soon as a good vacuum was obtained. The dry material was prepared by holding the apparatus at 60° for four days with the pumps operating continuously. A liquid-air trap was put into operation sometime before sealing off to remove mercury vapor.

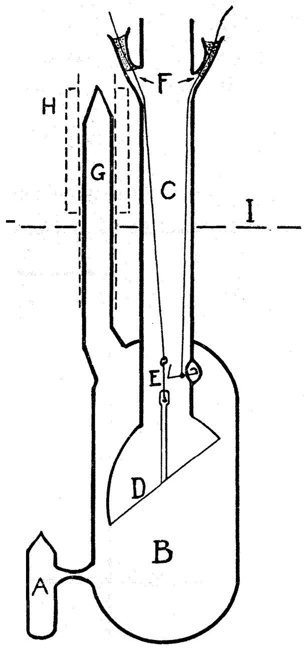


Fig. 2.

The data obtained are shown in Table I and the graph in Fig. 3. The figures given are in each case the means of several observations. The data obtained from the dried sample are indicated by asterisks. The results are in as good agreement as could be expected with the results of Johnson and Smith and Calvert, in view of the uncertainty in their measurements especially as regards temperature. The figures in Col. 4 are calculated from the equation $\log p = -(4402.1/T) + 10.1070$.

Table I

Vapor Pressure of Ammonium Chloride

	Temp., °K.	Obs. press., mm.	Log p (obs.)	Log p (calcd.)
1	557.0	159.63	2.2031	2.2030
2	546.1	111.19	2.0461	2.0460
3	523.2	49.47	1.6940	1.6940
4	507.1	26.46	1.4226	1.4260
5*	533.7	73.17	1.8643	1.8590
6*	532.6	69.76	1.8436	1.8400
7*	532.3	62.87	1.7984	1.8400
8*	529.9	63.63	1.8037	1.8010
9	532.5	69.31	1.8408	1.8410
10	471.3	5.93	1.7733	1.7660
11	501.3	21.68	1.3361	1.3250

The deviation is of the order of 1% except in the case of No. 7 and here there is reason to believe that the gage was not functioning properly. In

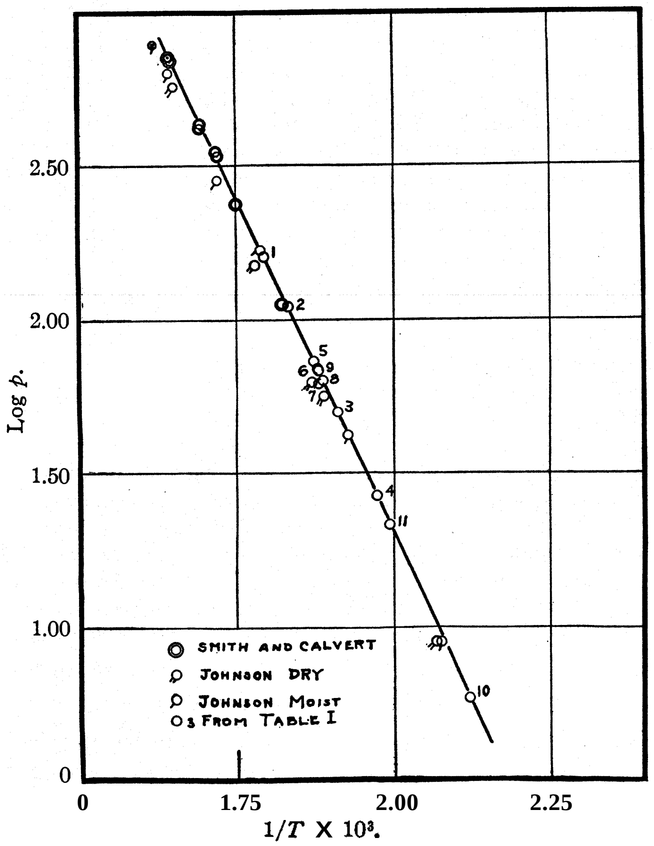


Fig. 3.

view of Johnson's results and ours there is no ground for believing that drying affects the vapor pressure of the salt. One effect of drying was unmistakable, however. This was the slowing up of the rate of evaporation and condensation. When the bulb contained moist salt and the Tube G was cooled the pressure fell very rapidly so that ten minutes would suffice for the pressure to fall to a value of a few mm., which corresponds to the transition temperature 184.3°, where the pressure would remain constant for some time. With the dried salt several hours would be required for all of the ammonium chloride to sublime out of the bulb and condense in the tube. So far as rate of evaporation and condensation were concerned the salt scarcely seemed to be volatile at all. This behavior would tend to confirm the reports that are to be found in the literature to the effect that gaseous ammonia and hydrogen chloride will not react when intensively dried. Another point requires comment. The heat of sublimation *per mole of vapor* as calculated from the vapor pressure equation above the transition point is 20,139. The heat of dissociation of solid ammonium chloride as measured calorimetrically is 41,900 Cal. per mole at 18°.[13] Allowing for a heat of transition of 970 Cal.,[14] but neglecting the difference in heat capacities of the solid and vapor, this gives a heat of sublimation above the transition point of 20,465 Cal. per *mole of vapor* for the completely dissociated salt. This figure is in such close agreement with the heat of sublimation obtained above from the vapor pressure equation that it is evidence in favor of complete dissociation for the vapor under all conditions. If the dissociation is not complete, then this agreement can only occur provided the heat of sublimation to the undissociated molecule be almost exactly half the heat of dissociation of the solid.

Vapor Density of **Ammonium** Chloride.—As was mentioned in the introduction to this paper, the experimental results on the vapor density of dried ammonium chloride which are given in the literature are not convincing. The methods which have been used are for the most part modifications of the Victor Meyer or Dumas methods. Neither of these methods is adapted for use in a determination where moisture is to be excluded or upon a substance which volatilizes slowly. The method of Knudsen[15] for the determination of vapor pressure by the rate of diffusion through an orifice is equally applicable to vapor density when the vapor pressure is known. This method has been used in this Laboratory for the determination of vapor pressures with success,[16] the only particular precaution necessary being that the surface of substance exposed be at least 100 times

---

[13] Thomsen, "Thermochemistry," Longmans, Green and Company, New York, **1908.**

[14] Bridgman, *Proc. Am. Acad.*, **52, 89** (1916).

[15] Knudsen, *Ann. Physik*, **29, 179** (1909).

[16] Rodebush and DeVries, THIS JOURNAL, 47, 2488 (1925); DeVries with Rodebush, *ibid.*, **49, 656** (1927).

the area of the orifice in order that the pressure of vapor in front of the orifice be kept at saturation. Such a method would seem to be ideal from the standpoint of intensive drying, since the solid salt will be subject to a continuous drying action during a run and successive runs should show a progressive drying effect, if such exists, in the apparent molecular weight. The apparatus is shown in Pig. 4.

The orifice was made by grinding away a tip drawn in the end of a pyrex tube. The edges of the orifice were very thin and the opening was nearly round. A large number of measurements of the diameter of the opening in different directions were made under a microscope with a step micrometer eyepiece. The diameter varied by only a small amount in different directions so that the area of the opening could be calculated with satisfactory accuracy. The orifice tube was sealed into the Bulb C, which was about 6 cm. in diameter. The ammonium chloride was introduced either directly or by sublimation from the side Tube B. The Bulb C was immersed in an oil-bath thermostat and a tube furnace was placed around the tube leading from the orifice to prevent premature condensation of the salt. During a run the ammonium chloride was condensed in the U-shaped bend T, which was surrounded by liquid air. The end of the tube was connected to the cascade of diffusion pumps and drying tubes.

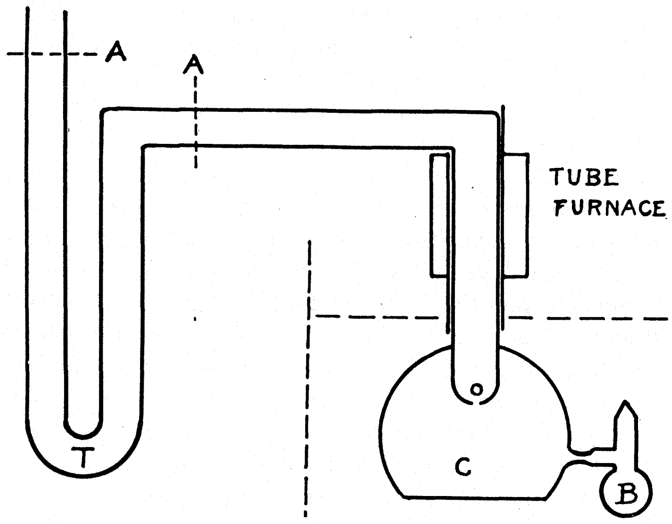


Fig. 4.

The temperature control was of the same accuracy as in the vapor pressure experiments and the same precautions were taken in the preliminary outgassing of the apparatus. In order to obtain a pressure low enough so that the simple kinetic theory could be applied to the process of effusion, it was necessary to work at temperatures below 100°. The pressures at these temperatures were calculated by means of the vapor-pressure equation, taking account of the heat of transition at 184.3 which has been determined by Bridgman[17] to be 970 cal. per mole. In making this calculation the vapor was assumed to be undissociated. The equation for rate of diffusion is

$$w = pat\sqrt{\frac{M}{2\pi RT}}$$

where w is the weight diffusing, p is the pressure in dynes, a is the area of the orifice, t is the time, M is the molecular weight, R is the gas constant in c. g. s. units and T is the absolute temperature. In case the vapor is not dissociated, this equation may be used directly to solve for the molecular weight. If the ammonium chloride is completely dissociated into ammonia and hydrogen chloride, it is easy to show that an apparent molecular weight will be obtained which is slightly different from the average for the two gases.

The preliminary drying was carried out in the manner previously described. When the apparatus was ready to begin a run it was brought to the desired temperature and the trap was immersed in liquid air. The time was noted with an accurate watch. The runs were of several hours duration. At the end of a run the trap was cut out of the apparatus at **A,** A, (Fig. 4) and the ammonium chloride was determined by precipitation of the chloride with silver nitrate. It was feared that the ammonia and hydrogen chloride might condense separately and escape on warming, so in several instances the trap was sealed off before the liquid air was removed, but no difference was noted in the results.

Results.—The results are shown in Table II. Except for No. 13, which is included for sake of completeness since the temperature got out of control during the overnight run, the results are uniformly low. Only one result is even high enough to correspond to complete dissociation. Since the surface of ammonium chloride exposed in the flask was more than 1000 times the area of the orifice, we are forced to conclude that a pronounced drying effect is obtained as soon as a vacuum is established, which slows up the rate of evaporation so that the pressure below the orifice falls below the saturation pressure. Even when moist ammonium chloride was introduced and the run started immediately the results obtained were low. When a preliminary pumping with the drying tubes was carried out, the results obtained were much lower still. If in extrapolating the vapor pressure to this temperature we had assumed complete dissociation, we should have obtained a higher pressure and consequently a still lower result would have been calculated for the apparent molecular weight. No conclusion may be drawn from these experiments as to the vapor density but the effect of drying on the rate of evaporation which was noticed in the vapor pressure

---

[17] Bridgman, *Proc. Am. Acad.,* **52**, 89 **(1916)**.

measurements is here confirmed in a positive manner. It must be noted that this slow rate of evaporation must be reckoned with in any method for the determination of vapor density.

TABLE II

MOLECULAR WEIGHT BY DIFFUSION METHOD

Run no.	Wt. diff., g.	Time, sec.	Temp., °K.	Press. mm. of Hg	Area of orifice, cm.^{2}	Mol. wt.	Remarks
4	0.1152	30960	369.33	0.0122	0.0218	21.2	No drying
5	.0985	35250	365.63	.00916	....	20.9	....
7	.0877	31260	365.42	.00910	....	21.5	....
10	.0932	38280	365.20	.00902	....	16.4	....
11	.0689	21600	365.42	.00910	....	27.7	....
12	.0837	31980	365.42	.00910	...	18.7	....
13	.1064	44100	358.86	.00521	....	47.6	Temp. out of control
14	.0202	24750	358.86	.00521	....	5.48	Dried with P_2O_5
15	.0154	29040	358.86	,00521	....	2.3	....
16	.0039	12840	358.86	.00521	....	0.76	....
17	.0178	21270	358.86	.00521	....	5.7	No drying
18	.0197	27000	358.86	.00521	....	4.37	....
19	.0278	44640	358.80	.00521	...	3.28	Dried with P_2O_5
20	.0122	17940	358.86	.00521	0.0149	8.1	No drying
21	.0119	15240	358.86	.00521	...	10.7	....
22	.0307	33260	358.86	.00521	....	14.9	....
23	.0131	16320	358.86	.00521	....	11.3	....

Vapor Density by the Microbalance

The determination of vapor density by means of the buoyancy effect upon a thin-walled bulb has been developed to a high degree of precision by Stock.[18] A microbalance patterned after the design of Stock was constructed of quartz (see Fig. 5). The balance was enclosed in a tube which was maintained at a temperature constant to 1° by a surrounding furnace which was regulated by automatic thermostatic control. The balance case was connected by a tube to a bulb which was surrounded by a second furnace with an independent automatic temperature control. When solid

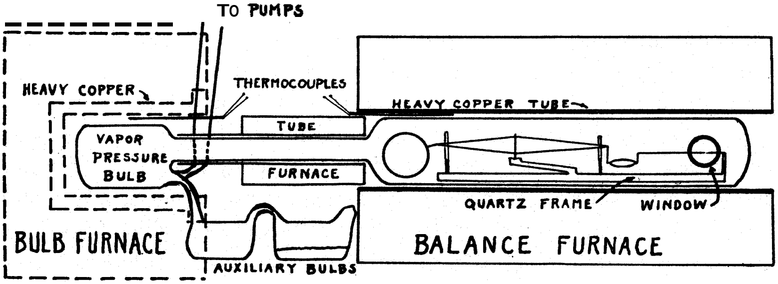


Fig. 5.

---

[18] Stock and Siecke, *Ber.*, 57,562 (1924).

ammonium chloride was placed in the bulb any desired pressure could be maintained in the balance case by varying the temperature of the bulb and hence the vapor pressure. This furnace could be held at a temperature constant to 0.1° for long periods.

Mode of Operation.—The apparatus was outgassed for ten hours at 480–500° under a high vacuum. The apparatus was then cooled and dried air introduced for the purpose of calibrating the balance. From the pressure and temperature the density necessary to bring the balance to the zero point was calculated by the gas laws. The data for the calibration are given in Table III. The two sets of figures given represent the extreme values of a series of determinations. A displacement of the pointer of 0.2 mm. corresponds to a change in density of about 0.001 g. per liter, and while it was possible to bring the pointer within 0.2 mm. of the zero position, accidental factors due to the high temperature and complicated apparatus caused a variation of an amount indicated by the figures in Table III. The temperature coefficient of the balance is negligible.

After the air had been removed, ammonium chloride was introduced into the vapor-pressure bulb and dried for ten days with the pump system operating continuously. The bulb containing the ammonium chloride was maintained at 60° and the rest of the apparatus at 300–400° during the drying operation.

A liquid-air trap was put into operation in the last twenty hours of drying. The apparatus was then sealed off according to the usual technique and the furnace brought to such temperatures that the density of the ammonium chloride vapor in the balance case was just sufficient to bring the balance to the zero point. The temperatures and corresponding vapor pressures for a series of observations are given in Table IV. In the fourth column are the apparent molecular weights as calculated by the gas laws from the pressures and temperatures. It will be seen that apparent molecular weights correspond to complete dissociation.

In order to be sure that complete equilibrium had been established between the vapor and solid, the apparatus was held at constant temperature

TABLE III

CALIBRATION OF MICROBALANCE *WITH* AIR

Pressure, mm.	**170**	**177**		
Temp., °K.	**587.8**	**588.8**		
Calcd. *d*, g./l.	**0.1346**	**0.1400**	**Av.**	**0.1373**

TABLE IV

VAPOR DENSITY OF AMMONIUM CHLORIDE

Vapor pressure bulb, °K.	**561.2**	**562.7**	**562.1**	**562.7**	
Vapor pressure	**183.6**	**192.3**	**188.8**	**192.3**	
Balance case temp., °K.	**593.3**	**596.9**	**598.0**	**588.0**	
Apparent mol. wt.	**27.7**	**26.6**	**27.1**	**26.2**	**Av. 26.9**

for twenty-four hours. When the temperature of the vapor-pressure bulb was changed by 1°, more than an hour was required for the resulting change in the microbalance pointer, showing again the effect of drying on the rate of establishment of equilibrium between vapor and solid.

Conclusions

It is impossible, of course, to assert positively that the ammonium chloride was sufficiently dried to produce the results reported by Baker and co-workers. It appears to the authors, however, that under the high vacuum and elevated temperature used in these experiments a few days' drying should be equal to several weeks by the methods used by previous workers in the field. The remarkable lag in the evaporation and condensation of the ammonium chloride observed in every case where the salt was dried would appear to be a satisfactory criterion of intensive drying. This slow vaporization would account for the high results obtained by Baker in his use of the Victor Meyer and Dumas methods, just as it caused low results in the effusion method as described in this paper. It must be remembered that Gutmann was not able to reproduce the work of Baker and that Johnson's results were contradictory. Smith and Lombard's results on the vapor density of the moist salt indicating incomplete dissociation are believed by the authors to be due to experimental error. In their determinations they distilled the salt into a bulb at constant temperature and the bulb was sealed off when filled with the saturated vapor. It seems likely that an excess of ammonium chloride was introduced into the bulb either by absorption on the glass surface or by mechanical convection. Smith argued that the vapor should be at the saturation pressure in order to show abnormal vapor density, but from the standpoint of thermodynamics there is nothing unique about the saturated vapor. In our experiments the temperature of the balance case was maintained 20–30" above the temperature of the vapor pressure bulb in order to avoid the adsorption of ammonium chloride on the microbalance. Since the largest area of surface was offered by the float bulb, adsorption would cause low results for the density. The temperature difference we believe would prevent any appreciable adsorption. On the other hand, if the dissociation is nearly complete at this temperature an extraordinary temperature coefficient would be required for any considerable reduction in the percentage dissociation at a temperature 25° lower. As has been pointed out earlier the hypothetical value for the heat of dissociation in the vapor phase is 20,000 Cal., which gives only a small temperature coefficient.

Summary

The vapor pressure of ammonium chloride is unaffected by intensive drying. This result confirms the work of previous investigators.

The rate of vaporization and condensation is affected to a remarkable degree by the state of dryness.

Ammonium chloride which has been dried for ten days at 60° in a high vacuum appears to be completely dissociated in the vapor state.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS. I. THE SONIC INTERFEROMETER. THE VELOCITY OF SOUND IN SOME ORGANIC LIQUIDS AND THEIR COMPRESSIBILITIES[1]

BY EGBERT B. FREYER[2] WITH J. C. HUBBARD AND DONALD H. ANDREWS

RECEIVED OCTOBER 27, 1928 PUBLISHED MARCH 6, 1929

A number of investigators[3] have studied the velocity of sound in liquids at audible frequencies but the methods are beset with so many difficulties and involve the use of such large quantities of liquids that few results of adequate precision for thermodynamic treatment have been obtained. More recently[4] the field of high frequency sound production using piezoelectric crystals has been entered, and Hubbard and Loomis[5] have developed a method which has yielded very accurate values for the velocity of sound in liquids. The investigation recorded here was conducted according to their method and is a part of the general program of thermodynamic research on organic compounds now being undertaken at this Laboratory. The sonic interferometer has been further developed with especial reference to temperature control, the prevention of evaporation of the liquid being studied and of contamination by water vapor from the air.

Apparatus and Method

The electrical equipment is shown in Figs. 1, 2 and 3. When the circuit Y is tuned by means of the condenser (15), a heterodyne is produced between the two oscillating circuits. When the note is made to coincide in pitch with that produced by the tuning fork, the crystal in the interferometer is known to be vibrating with the same frequency

---

[1] This paper was presented in part at the Swampscott meeting of the American Chemical Society in September, 1928.

[2] From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Schmidt, *Wiener* **Ber.**, (IIa) **114, 945 (1905);** Dorsing, "Inaug. Diss.," Bonn, **1907; Ann.** *Physik,* **[4] 25,227 (1908);** Busse, *ibid.*, **75,657 (1924);** Pooler, *Phys. Rev.,* **31, 157 (1928)** (abstract).

[4] Boyle, *Trans. Roy. Soc. Canada,* **17,141 (1923); 159,191, 197 (1925); 79 (1927)**; Langevin, British Patent Spec. N. S. **457,** No. **145,691 (1920).**

[5] Hubbard and Loomis, **Nature, 120, 189 (1927);** *Phys. Rev.,* **31, 158 (1928);** *Phil* **Mag., VII,** *5,* **1177 (1928).**

as circuit X[6] (this being fixed and determined by crystal (7)), plus or minus 1000 cycles, the frequency of the fork. Exact coincidence of the two audible frequencies is indicated by the disappearance of the easily discernible beats heard when the fork is operated.

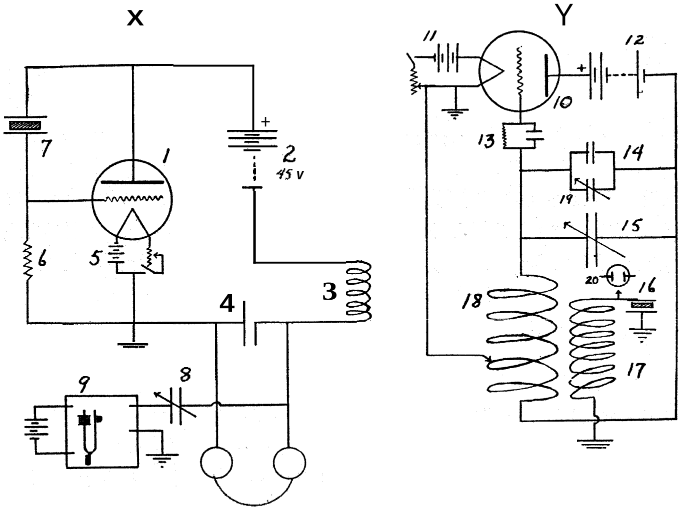


Fig. 1.—X, ***The Pierce Oscillator:*** 1, *UX*, 199 tube; 2, 45 volts; 3, choke, 30 millihenries; 4, 0.002 mf.; 5, two dry cells in series; 6, grid leak, 1 megohm; 7, crystal, see Fig. 2; **8**, 0.0005 mf.; 9, 1000-cycle electrically driven tuning fork (General Radio). Y. ***The Hartley Oscillator:*** 10, UX–171 or UX–210 tube; 11, 7 volts, D. C.; 12, 180 to 300 volts D. C.; 13, grid leak, 1 megohm; 0.002 mf.; 14, 1 to 3 mf. (so arranged that 1, 2 or 3 mf. may be used); 15, 0.001 mf.; 16, sonic interferometer, see Fig. 3; 17, 60 to 90 turns of No. 25 B. and S. insulated copper wire, wound closely, diameter of coil, 4"; 18, 30 turns of No. 16 B. and S. bare copper wire, coil 5" in diameter, 6" long, alternate turns provided with projections to clip onto; 19, two plate vernier condenser; 20, neon lamp, see Fig. 4.

The final tuning is effected by means of the vernier condenser. Assuming the lower surface of the interferometer piston to be in a nodal plane, *i. e.*, assuming a system of "stationary waves" in the liquid, the beats will return if the piston is raised or lowered even a very slight distance (0.002 mm.). By a proper simultaneous manipulation of

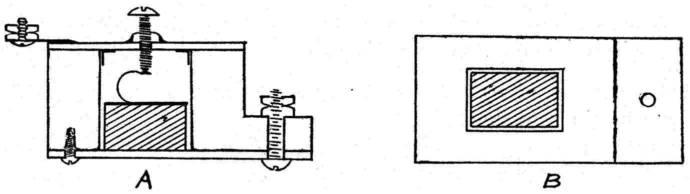


Fig. 2.—Housing for control crystal (7) in Fig. 1.

---

[6] G. W. Pierce, *Proc. Am. Acad.*, *60*, 269 (1925). For other circuits see *Proc. Inst. Radio Eng.*, **15**, 9 (1927).

the vernier condenser and the micrometer screw on the interferometer the nodes are located and their relative positions read from the micrometer screw scale. A reading of the screw setting is taken when the beat frequency is zero (piston in node); calling this reading x, and lowering the piston through the liquid for a distance of about two centimeters, counting meanwhile the number of nodes, n, a second screw reading, y, is taken for the position of another node. Then $(x - y)/n = \lambda/2$ and $2\omega \times (x - y)/n = v$, where ω is the frequency of oscillator Y, and v is the velocity of sound in the liquid.

The accompanying drawings illustrate the essential details of the apparatus. Brief mention may be made of the experimental arrangement.

The circuits were mounted on a board bearing a hard rubber panel supporting the condensers and rheostats; this was in turn mounted in a copper-lined box for shielding. The control dials were placed on the outside of this box to be within easy reach. As measurements were made in a number of different thermostats, the entire apparatus was made portable. The box was screwed to the top of a table mounted on rubber-tired casters. Several inches from the floor was a large shelf supported by the table legs; this carried all of the batteries. These and the leads to the circuits above them were shielded by enclosing the whole in copper window screening, using the table to support this. The wire leading from the secondary coil to the sonic interferometer was shielded by running it through a brass tube three centimeters in diameter by thirty centimeters long. It was attached to the side of the box through a universal joint. The lead was maintained rigid in the tube by having it pass through a glass tube supported at either end by corks. As there was a considerable potential between this wire and the shielding (about 1000 volts if a UX 210 tube is used), a pronounced condenser action resulted between the two; to keep this at a minimum, the lead was as short as possible and not too close to its shielding. Contact with the interferometer was made by a clip on the same, the contact itself being shielded by a sheath which slid over the brass tube bearing the lead.

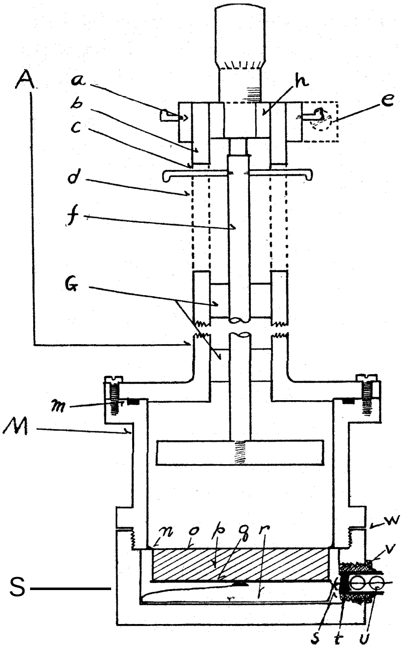


Fig. 3.—*The* **Sonic** *Interferometer:* Materials: *A*, bronze; *M*, iron; *S*, bakelite; f, "Invar" steel; *a*, *e*, clamp; *b*, four vertical slots, not shown; c, hook for rubber bands; *d*, slot; *g*, guide collars; m, rubber gasket, slightly thicker than depth of groove; *n*, Solder; o, phospho-bronze, 0.005" thick; *p*, quartz disk; *q*, bronze or brass; *r*, spring; *s*, good contact; *t*, deKhotinsky; *u*, glass beads; *v*, brass bushing into which is soldered the copper tube bearing the lead wire; *w*, water-tight seal. The piston and inside of the cup were gold plated.

An alternate, though less precise, method of detecting the nodes involves the use of a neon lamp (20). This was mounted in a tube as shown in Fig. 4; whenever the circuit was oscillating, the lamp exhibited a red glow. When the piston was exactly in a node, however, the glow either disappeared entirely (owing to the drop in the value of the current) or so changed in shape and intensity that there was no mistaking the position of the node as read on the micrometer screw. Even when this device was not used for the precise determination of the separation of the nodes, it very conveniently served as an indication of when the circuit was oscillating. The character of the glow was determined by the distance between strip (a) and the lamp. Cemented to the screw was a glass tube to insulate the high tension wire against the hand when adjustments were made. In general, for detecting nodes, the distance (a) was such that the glow was quite faint when the piston was *not* in a node. The lens rendered a better view of the glow. The device was mounted by a universal joint to the top of the box containing the circuits and could thus be made visible from any angle.

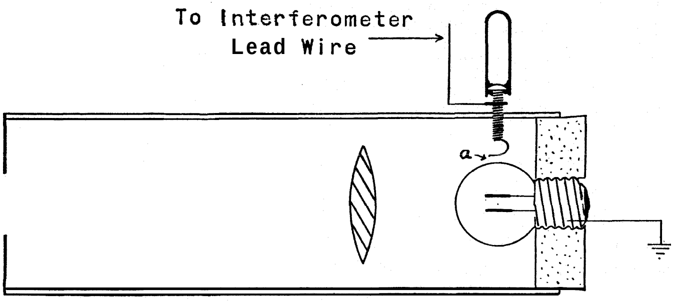


Fig. 4.

Materials.—With a few exceptions the samples studied in this investigation were prepared as follows: "Baker's C.P. Analysed" liquids were distilled through a three-foot punched-in column, only those cuts being taken for measurement that boiled within 0.1" of the latest published boiling points. Appropriate barometric and stem corrections were made. Those liquids that tend to dissolve water vapor were carefully dried and protected during storage. The glycerin (Baker's Analysed) was dried for several hours at water-bath temperature through phosphorus pentoxide. The purity of the bromoform and α-bromonaphthalene was questionable, but these liquids were included in the investigation only because they, like benzene, melt at a convenient temperature and it was desired to ascertain if the break in the velocity of the sound–temperature curve, noticed first in the case of benzene, was a phenomenon of general occurrence. The isomeric heptanes were prepared in the research laboratory of the Ethyl Gasoline Corporation and kindly loaned to us for use in this investigation.

Sources of Error and the Precision.—A possible source of error was the absorption of water vapor from the air during the actual measurement. This apparently was quite appreciable in the case of acetone, as manifested by the difference between two readings made an hour and a half apart. It was avoided by using a fresh sample of the liquid for each measurement. This error was borne in mind throughout the investigation and appropriate precautions were taken to avoid it. A new design of the spring mechanism on the piston entirely eliminates this source of error by closing up the slots (d).

For some reason not yet ascertained the oscillations were considerably weakened at temperatures above 50° and with some liquids they disappeared entirely. The values given for the velocity of sound at this temperature are extrapolated ones. If an air bubble is entrapped under the piston when it is inserted, the sonic "reaction" may be greatly weakened or entirely absent.

As a rule screw readings were taken on three or four adjacent nodes when the piston was near the upper limit of its range and three or four when it was near the lower limit, the number of nodes in the interval being, of course, known. Occasionally, however, the position of each node was determined, as sometimes the $\lambda/2$ value between two nodes near the center of the liquid column would be a freak one, differing for no apparent reason from all of the others. Such a value was ignored in averaging the values of $\lambda/2$. It is felt that this procedure was justified, considering the close agreement between all of the normal values and the great discrepancy between the normal ones and the "freak" datum, as illustrated in a sample determination shown in Table I.

TABLE I

SAMPLE DETERMINATION

Alcohol at 20° (A)

Screw reading, x mm.	Diff. = $\lambda/2$	Screw reading, y mm.	Diff. = $\lambda/2$	$x - y$	$\frac{x-y}{n} = \frac{\lambda}{2}$
18.085		**6.590**		**11.495**	**1.4370**
	1.440		**1.445**		
16.645		**5.145**		**11.500**	**1.4375**
	1.440		**1.440**		
15.205		**3.705**		**11.500**	**1.4375**
	1.440		**1.440**		
13.765		**2.265**		**11.500**	**1.4375**

$$V = 2\frac{\lambda}{2}\omega = 1168 \text{ m./sec.}$$

Benzene at 35° (B)

Screw reading	**19.460**		**17.910**		**16.365**		**14.814**		**13.270**		**11.722**
Difference		**1.550**		**1.545**		**1.551**		**1.544**		**1.548**	
Screw reading	**11,722**		**10.175**		**8.625**		**7.105**		**5.553**		**4.008**
Difference		**1.547**		**1.550**		**(1.520)**		**1.552**		**1.545**	

Mean difference, 1.548. V = 1254 m./sec.

As the data in the last column of (A) represent a precision greater than could be attained using different samples of a liquid, only four significant figures are retained for the most part in the final value of the velocity of sound. Usually independent measurements gave results that checked to one meter per second. The velocity of sound in water, for example, was found on two different occasions to be **1498.6** and **1498.3** m./sec. The average of a large number of determinations by Hubbard and Loomis with a different interferometer and at a different frequency gave **1498.1.** The former figures were obtained without making any special effort to attain the maximum precision of which the method is capable.

Mention should be made of the behavior of the frequency control crystal during these measurements. The crystal and its principal frequency calibration was furnished by the Naval Research Laboratory. In addition to the principal frequency, the crystal exhibited others, as is usually the case: a parallelopipedal oscillator may vibrate along three axes under proper circumstances, each of these periods may have overtones and the crystal may also oscillate with a period which results from the coupling of vibration of two of these modes. When these "overtones" are present they are quite definite and sharp (but easily distinguishable from the fundamental by the character of the audible heterodyne note). At one time, however, the constants of the circuit were such that abrupt changes in frequency occurred, the crystal vibrating now in one, now in the other, fundamental frequency. A careful check showed which liquids had been measured on the new frequency and its value was established in the following manner. Six careful determinations of the wave length in several different samples of pure, air-free distilled water were made. From the accurately known values of the velocity of sound in water-at the temperatures of measurement[5] the frequency was calculated. The velocity of sound values used were taken from a curve drawn through a large number of points (about 50) in a 40° temperature interval. They are believed to be accurate to one part in ten thousand. The values of the frequency thus found are as follows: 414.0, 414.1, 414.3, 414.1, 413.8, 413.8—mean, 414.0(1) kilocycles.

These were checked to about 1% with a wavemeter, and, further, at different intervals of time by other sound wave-length determinations. The definiteness and constancy of the new frequency was thus firmly established.

Results and Calculations.—In the following tables are given the

TABLE II

VALUES OF THE ISOTHERMAL COMPRESSIBILITY AND C_p/C_v CALCULATED FROM THE VELOCITY OF SOUND, ETC.

Temp., °C.	Vel. of sound m./sec.	ρ	dv/dT	C_p	β_T, atm.$^{-1}$ $\times 10^6$	C_p/C_v	$\beta_\phi \times 10^6$ Tyrer	B_φ (F., H. and A.) Atm.$^{-1}$ $\times 10^6$
				Benzene				
0		0.9001	0.00131	0.3970			56.6	
10	1375	.8896	.00134	.4027	87.5	1.449	61.3	60.3
20	1324	.8790	.00138	.4084	94.9	1.441	66.3	65.8
30	1278	.8684	.00142	.4141	102.5	1.435	71.7	71.5
40	1231	.8576	.00146	.4196	111.0	1.422	77.8	78.0
50	1184	.8467	.00151	.4255	119.9	1.420	84.6	85.4
				Alcohol				
0	1242	0.8062	0.001286	0.5487	97.6	1.196	83.5	81.5
10	1204	.7978	.001325	.5706	104.4	1.191	89.8	87.6
20	1168	.7893	.001370	.5950	111.3	1.183	95.7	94.1
30	1134	.7809	.001420	.6208	119.6	1.184	102.0	101.0
40	1101	.7722	.001475	.6478	127.8	1.181	109.0	108.2
50	1067	.7632	.001550	.6762	137.8	1.182	116.7	116.6

TABLE II *(Continued)*

Temp., °C.	Vel. of sound m./sec.	ρ	dv/dT	C_p	β_T, atm.$^{-1}$ $\times 10^6$	C_p/C_v	$\beta_\phi \times 10^6$ Tyrer	B_φ (F., H. and A.) Atm.$^{-1} \times 10^6$
Acetone								
0	1273	0.8125	......	....	...	...	...	77.0
10	1231	.8014	......	....	...	...	...	83.5
20	1190	.7905	0.001881	0.514	129.2	1.426	...	90.6
30	1146	.7788	......	....	...	...	...	99.1
40	1102	.7672	0.002122	.530	158.2	1.456	...	108.8
50	1057	.7554	......	....	...	...	...	120.1
Chlorobenzene								
0	1362.5	0.8666	0.000850	....	...	...	49.05	47.3
10	1322.5	.8952	.000867	....	...	...	52.30	51.9
20	1284.5	.9040	.000880	0.315	74.8	1.348	55.7	55.5
30	1248.0	.9129	.000895	.322	79.4	1.338	59.4	59.4
40	1212.5	.9220	.000910	.328	84.3	1.325	63.4	63.6
50	1178.0	.9309	.000925	.335	89.5	1.316	67.8	68.0
Toluene								
0	1414	0.8848	0.00124	0.3834	80.8	1.410	59.6	57.3
10	1370.5	.8752	.00125	.3938	85.5	1.388	62.9	61.6
20	1327.5	.8657	.00126	.4042	90.6	1.364	67.4	66.4
30	1284.5	.8563	.00127	.4147	96.2	1.340	72.3	71.8
40	1242	.8470	.00129	.4251	102.7	1.323	77.4	77.6
50	1199	.8378	.00132	.4355	110.4	1.311	83.2	84.2
Chloroform								
0	1069.0	1.5264	0.000810	0.2323	86.6	1.490	58.8	58.1
10	1036.5	1.5078	.000830	.2333	93.1	1.487	63.4	62.6
20	1002.5	1.4888	.000855	.2343	100.7	1.485	68.3	67.8
30	967.5	1.4697	.000884	.2353	109.5	1.486	73.5	73.7
40	932.5	1.4505	.000917	.2363	119.5	1.486	79.4	80.4
50	897.0	1.4310	....	....	...	...	...	...
Ether								
0	1095	0.7362	0.00203	0.5290	152.7	1.330	114.5	114.8
10	1054	.7248	.002115	.5349	167.4	1.330	127.5	125.8
20	1006	.7135	.002245	.5527	186.8	1.329	141.0	140.6
30	949	.7019	.002390	.5645	210.8	1.328	156.0	158.7
Carbon Tetrachloride								
0	1008	1.6327	0.000730	.2010	89.7	1.468	62.8	61.1
10	970	1.6134	.000742	.2013	97.0	1.452	67.4	66.8
20	935	1.5939	.000756	.2016	104.8	1.439	72.5	72.8
30	904	1.5748	.000777	.2019	113.3	1.437	78.1	78.8
40	873.5	1.5557	.000805	.2022	123.2	1.433	84.2	85.4
50	843	1.5361	.000837	.2025	134.4	1.427	91.1	92.9
Carbon Disulfide								
0	1223.5	1.2931	0.000880	0.2352	80.5	1.536	52.9	52.4
10	1190.5	1.2783	.000908	.2368	86.5	1.544	56.3	56.0
20	1158.0	1.2634	.000941	.2385	93.1	1.556	60.0	59.8

TABLE II (*Concluded*)

Temp., °C.	Vel. of sound m./sec.	ρ	dv/dT	C_p	β_T, atm.$^{-1}$ $\times 10^6$	C_p/C_v	$\beta_\phi \times 10^6$ Tyrer	B_φ (F., H. and A.) Atm.$^{-1}$ $\times 10^6$
30	1126.0	1.2483	.000983	.2401	100.9	1.574	63.8	64.1
40	1093.5	1.2327	.001036	.2417	110.3	1.603	68.4	68.8
50	1061.0	1.2168	.001097	.2433	121.1	1.636	73.9	74.0
			Methyl Alcohol					
0	1187	0.8100	0.001468	0.563	109.2	1.230	...	88.8
10	1154	.8007	.001505	.594	116.0	1.221	...	95.1
20	1121	.7913	.001554	.632	123.4	1.211	...	101.9
30	1088	.7818	.001609	.679	131.5	1.199	...	109.6
40	1056	.7723	.001670	.732	140.0	1.189	...	117.7
50	1023.5	.7627	.001741	.793	149.6	1.180	...	126.8

Temp., °C.	Vel. of sound, m./sec.	ρ	B_φ (F., H. and A.) atm.$^{-1}$ $\times 10^6$
	Heptane		
0	1235	0.7005	94.9
10	1196	.6920	102.4
20	1154	.6836	111.4
30	1112	.6751	121.4
40	1070	.6665	132.8
50	1028	.6579	145.8
	Octane		
0	1277	0.7185	86.5
10	1235	.7103	93.6
20	1192	.7021	101.6
30	1150	.6940	110.4
40	1108	.6859	120.4
50	1066	.6777	131.6
	Aniline		
0	1742	1.0389	32.2
10	1700	1.0303	34.0
20	1659	1.0216	36.1
30	1619	1.0130	38.2
40	1579.5	1.0044	40.5
50	1540	0.9957	42.9

Temp., °C.	Vel. of sound, m./sec.	ρ	B_φ (F., H. and A.) atm.$^{-1}$ $\times 10^6$
	α-Bromonaphthalene		
10	1402	1.503	34.3
20	1372	1.487	36.2
30	1341	1.472	38.3
40	1311	1.459	40.4
50	1280	1.448	42.7
	Glycerin		
10	1941.5	i.2671	22.2
20	1923	1.2613	21.7
30	1905	1.2553	22.3
40	1886.5	1.2491	22.8
50	1868.5	1.2427	23.4
	Bromoform		
10	953	2.886	38.7
20	928	2.858	41.2
30	907	2.830	43.5
40	886	2.802	46.1
50	865	2.774	48.8

	Vel. of sound, 45°	Vel. of sound, 20°	d_4^{20}	β_φ at 20°, atm.$^{-1}$ $\times 10^6$
n-Heptane	1048	1154.0	0.6836	111.40
2-Methylhexane	1014	1120.0	.6789	119.05
3-Methylhexane	1033	1135.5	.6870	114.45
3-Ethylpentane	1061	1169.5	.6982	106.15
2,2-Dimethylpentane	972	1080.5	.6737	128.90
2,3-Dimethylpentane	1039	1148.5	.6942	110.70
2,4-Dimethylpentane	984.5	1083.5	.6745	128.00
3,3-Dimethylpentane	1024.5	1129.5	.6935	114.55
2,2,3-Trimethylbutane	1000	1101.5	.6901	121.05
2,2,4-Trimethylpentane	998.5	1098.5	.6918	121.45

TABLE III

COMPARISON OF ISOTHERMAL COMPRESSIBILITIES OF BENZENE AND ETHYL ALCOHOL FROM VARIOUS SOURCES

Temp., °C.	F, H. and A. (1 atm.)	Tyrer 1–2 atm.	Pagliano and Palazzo[a] (1–4 atm.)	Röntgen[b] (8 atm.)	Amagat[c]
			Benzene		
17.9	...	...	...	91.7×10^{-6}	...
20	94.9×10^{-6}	95.3×10^{-6}	90.1×10^{-6}	...	...
40	111.0	110.7	105	...	...
			Ethyl Alcohol		
0	97.6	99.6	97	...	100×10^{-6} (extrpd.)
10	104.4	106.6	...	...	...
14	...	...	...	...	101
20	111.3	112.9	105.3	...	115 (extrapolated)
40	127.8	128.6	117.8	...	129

[a] Pagliano and Palazzo, Ann. Phys. *Chem.*, (iii) 44, 1 (1891).

[b] Rontgen, *Mem. accad. Lincei,* (vi) 19, 30 (1883).

[c] Amagat, Ann. *chim. phys.,* 29, 523 (1893).

results of the velocity of sound measurements and the compressibilities and compressibility ratios calculated from them.[7]

The blanks are due to the absence of certain specific heat and coefficient of expansion data. It is hoped to fill these soon by measurements to be undertaken in this Laboratory. The density, specific heat and coefficient of expansion values used were the same as those used by Tyrer,[8] in the cases where comparison is made of the measured adiabatic compressibility data with those calculated from the velocity of sound. They are believed to be very trustworthy. Those not from this source were taken from the Landolt-Bornstein "Tabellen" and the "International Critical Tables." Table III is given to indicate briefly how the calculated compressibilities compare with those experimentally determined. In Figs. 5 and 6 are shown the velocities of sound and adiabatic compressibilities plotted against temperature. Tyrer's values for the compressibility of ether are included, since the compressibility data from the two sources for this liquid show a greater disagreement than do the data for any of the other liquids.

Attention is called to the slight deviation from linearity of the velocity of sound curve for benzene in a short temperature range just above the melt-

---

[7] The following are the equations used

$$V = \sqrt{\frac{1}{\beta_\varphi \rho}} \qquad \beta_T = \beta_\varphi + \frac{\left(\frac{dv}{dT}\right)^2 \rho T}{JC_p} \qquad \frac{C_p}{C_v} = \frac{\beta_T}{\beta_\varphi}$$

where V is the velocity of sound; β_φ is the adiabatic compressibility; β_T is the isothermal compressibility; dv/dT is the differential of the specific volume; J is the mechanical equivalent of heat; ρ is the density; C_p is the specific heat at constant pressure at $T°$ absolute.

[8] Tyrer, J. *Chem. Sec.*, 103, 1684 (1913).

ing point. This behavior suggested the measurements on aniline, bromoform, a-bromonaphthalene and glycerin. Except in the case of glycerin, somewhat similar breaks in the curves occur. The glycerin did not freeze.

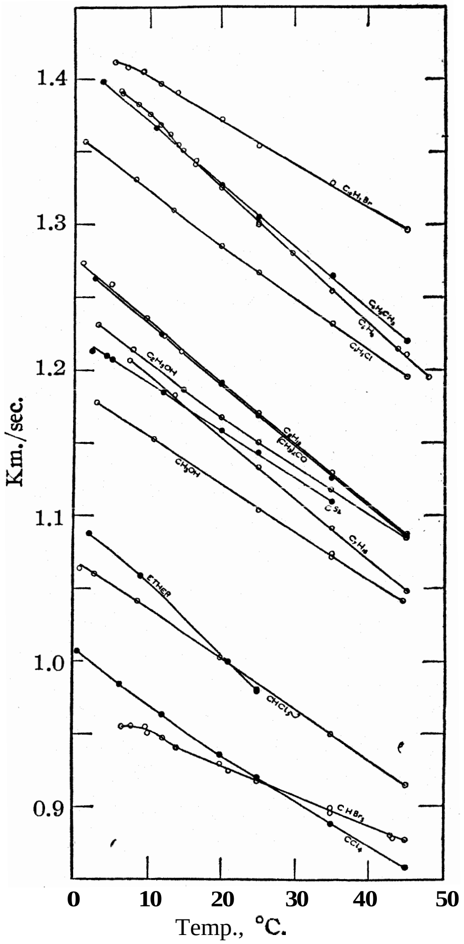
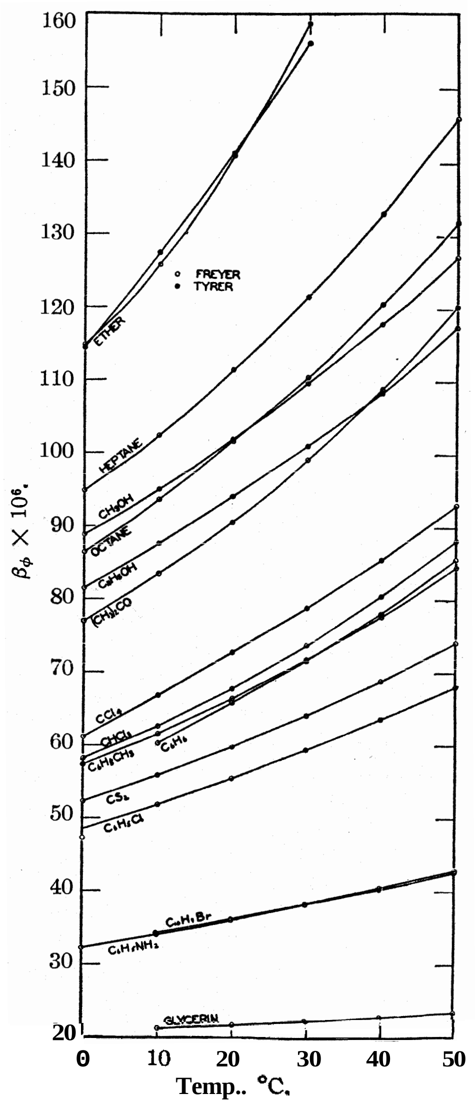


Fig. 5.



Pig. 6.

It seems reasonable to expect some sort of orientation or grouping of the molecules of liquids to occur preliminary to freezing that would occasion such a change, because the velocity of sound in a liquid is a function of properties directly depending on the molecular arrangement.

Discussing the dipole character of liquids, Gerlach[9] observes, "Dipoles, by their very nature, are favorable to association—after a fashion—a preliminary stage of microcrystalline character; .... it is not definitely known whether such a character is in evidence during the solidification of substances like benzol whose molecules exhibit not even the slightest dipole nature. Attention may be directed in this connection to certain experiments of Isnardi in which he has observed variations in the dielectric constant of benzene at temperatures slightly above its crystallization point. This would indicate, under such conditions, the existence of a dipole moment, but since Graffunder's results fail to confirm such a conclusion, further experimental evidence must be awaited." Unfortunately the compressibility measurements of Tyrer[8] do not cover the temperature range in question in sufficient detail to permit a confirmation of this irregularity in the velocity of sound in benzene by calculation.

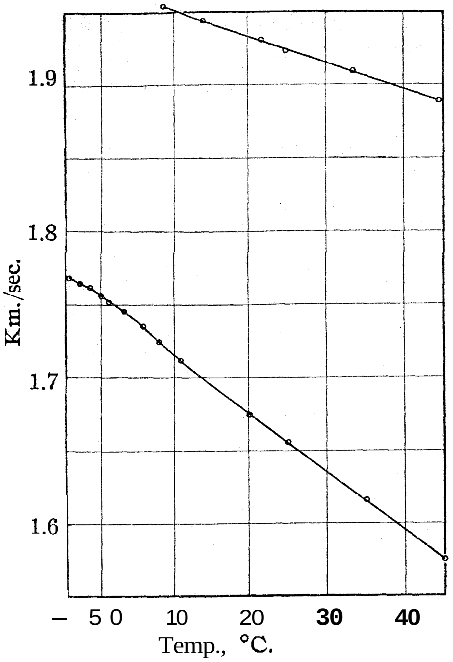


Fig. 7.—Upper curve, glycerin; lower curve, aniline.

The authors are indebted to Mr. Alfred L. Loomis for the use of quartz plates in the interferometer and to the U. S. Naval Research Laboratory for supplying the calibrated quartz frequency control crystal. Grateful acknowledgment is made to Dr. Graham Edgar of the Ethyl Gasoline Corporation for the loan of the isomeric heptanes and for the values of their densities.

Summary

An explanation of the method developed by Hubbard and Loomis for measuring the velocity of sound in small quantities of liquids has been given. The apparatus consists of an electrical oscillator for producing a high frequency field, an oscillator of fixed frequency to control the frequency of the field, and a "sonic interferometer" for producing and determining the wave length of sound waves. The instrument described in this paper is of a new design. The velocity of sound in and the adiabatic

---

[9] Gerlach–Fuchs, "Matter, Electricity, Energy" (Translation), 1928, p. 65.

and isothermal compressibility of the following liquids are given: benzene, acetone, ethyl alcohol, methyl alcohol, chlorobenzene, toluene, chloroform, ether, carbon tetrachloride and carbon bisulfide.

The velocity of sound in and the adiabatic compressibility of heptane, octane, aniline, α-bromonaphthalene, glycerin, bromoform and the isomeric heptanes are given.

Some of the compressibility values have been compared with those found by direct measurement by other investigators.

BALTIMORE, MARYLAND

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

THE PHOTOSYNTHESIS OF HYDROCHLORIC ACID AT LOW PRESSURES

BY GERHARD K. ROLLEFSON

RECEIVED OCTOBER 29, 1928 PUBLISHED MARCH 6, 1929

The mechanism of the photochemical combination of hydrogen and chlorine has been the subject of investigation for many years. The results prior to 1926, summarized by Thon,[1] show that the reaction which occurs with the visible and near ultraviolet light must be considered as proceeding according to a chain mechanism starting with the photo-activated chlorine. The nature of this activation has been the subject of speculation, and the assumptions which have been made fall into two groups; first, those that postulate that the light excites the chlorine molecule to a higher quantum state; second, those that consider that the chlorine molecule is dissociated by the light. From the nature of the absorption spectrum of chlorine the dissociation hypothesis is the more probable of the two,[2] and it is the purpose of this paper to present experimental evidence for this view.

Before describing the experimental procedure let us consider what conditions are necessary to show a difference between the two theories. If we have an excited chlorine molecule it may undergo one of the following changes: (1) return to its normal state by emitting light, (2) lose its energy by collision of the second kind, (3) enter into some reaction. At high pressures an excited molecule undergoes so many collisions in its life period that the number returning to the normal state by fluorescence is negligible, but as the pressure is reduced the number fluorescing increases until, at such low pressures that the time between collisions is long compared to the life period of the excited molecule, fluorescence is practically the only process involved. On the other hand, if the chlorine is dissociated

---

[1] Thon, *Fortschritte Chem., Physik, physik. Chem.*, *18*, No. 11 (1926).

[2] For this interpretation of the chlorine spectrum see Franck, *Trans. Faraday Soc.*, 21, 536 (1925); and Kuhn, *Z. Physik*, 39, 77 (1926).

by light into a normal and an excited atom in the $^2P_1$ state[2] the possibility of fluorescence is eliminated[3] and the life periods of the normal and excited atoms are so long that even at low pressures there remains a great probability that they will enter into reaction. Therefore, if we study the photochemical reaction rate at various pressures, we should find that the velocity constant would decrease rapidly at very low pressures if the active form of the chlorine is an excited molecule, but if the active substance is a normal or an excited chlorine atom the velocity constant should be independent of the pressure.

The pressure at which this difference should appear may be estimated with the aid of the kinetic theory. The number of collisions which a molecule suffers in a mixture of two gases is given[4] by

$$Z_1 = \sqrt{2N_1}\pi\sigma_1{}^2\bar{C}_1 + \sqrt{\frac{m_1 + m_2}{m_2}}\, N_2\pi\sigma_2\bar{C}_1$$

where Z_1 is the total number of collisions per second for a molecule of Type I, N_1 is the number of molecules of Type 1, N_2 the number of Type 2, $\bar{C}_1$ is the mean velocity of the molecule of Type 1, σ_1 the diameter of the molecule of the first kind and σ_2 the average molecular diameter of the two kinds of molecules. The first term represents the number of collisions of the molecule with other molecules of the same kind, the second term gives the number of collisions with those of the other kind. It readily follows that the time between collisions of a chlorine molecule with a molecule of another kind is given by

$$\frac{1}{\sqrt{\frac{m_1 + m_2}{m_2}}\, N_2\pi\sigma^2\bar{C}_1}$$

The only uncertain quantity in this expression is a, the molecular diameter, and it is sufficiently accurate for this calculation to assume a value of 3×10^{-8} cm. At a pressure of 0.1 mm. of the other gas the time between collisions is 7.6×10^{-7} sec. According to the work of Wien[5] and Kerschbaum,[6] the life periods of atoms in excited states, which are not metastable, range from 0.1 to 1.5×10^{-7} sec. It seems reasonable to assume that the life period of an excited chlorine molecule is of the same order of magnitude and, therefore, if we are dealing with a reaction between an excited chlorine molecule and some other molecule, we should expect the rate

---

[3] The transition from the $^2P_1$ to the $^2P_2$ state of the chlorine atom with emission of light is forbidden by the selection principle for azimuthal quantum numbers. The other possibility. namely, the recombination of the normal and excited atoms with the emission of light can be neglected since the extremely low concentrations of the two kinds of atoms make the probability of such a transition extremely slight.

[4] Geiger and Scheel, "Handbuch der Physik," Springer, Berlin, 1926, Vol. IX, p. 399.

[5] Wien, Ann. *Physik,* 83, 1 (1927).

[6] Kerschbaum, *ibid.,* 83, 287 (1927).

constant to decrease rapidly as the pressure of the other molecules was reduced below 1 mm.

In the particular reaction under consideration the active form of the chlorine must react either with water or hydrogen. For reasons which will be given later the reaction with water seems to be the more probable, but since it is not definitely established the effect of varying both the hydrogen and water vapor pressures must be considered. Coehn and Jung[7] found that the rate of the reaction is independent of the pressure of water vapor down to 10^{-5} mm. It follows immediately that if the first step in the chain mechanism is a reaction between the active chlorine and a water molecule, the active form of the chlorine cannot be an excited molecule, as the life period of such a molecule would be very much shorter than the time between collisions with water molecules. It remains to be shown that the same is true if the active chlorine reacts with *a* hydrogen molecule.

In order to make the effect of diminishing pressure on the rate easy to detect, it is desirable to have the rate equation as simple as possible. From the work on the reaction between H_2 and Cl_2 at high pressures, we know that if the chlorine is much in excess the reaction follows the law

$$\frac{d(HCl)}{dt} = -2\,\frac{d(H_2)}{dt} = KI_0(H_2)(Cl_2)$$

By keeping the Cl_2 pressure constant or putting in so much chlorine that the change in pressure may be neglected, this equation may be integrated to give

$$\log (H_2) = -Kt + a$$

where K includes the chlorine pressure, the light intensity and any numerical constants, and a is the constant of integration. Now if we are dealing with active molecules, K will not be constant as the pressure is lowered, whereas if the chlorine is dissociated it will be constant over the entire pressure range down to 0.001 mm. pressure of H_2 and probably lower, although the accuracy of the measurements decreases rapidly at lower pressures.

Experimental

The reaction was studied by illuminating the mixture of the moist gases in a pyrex glass bulb of about 300 cc. capacity with white light from a 100-watt tungsten filament lamp placed about 2 cm. from the reaction chamber. At intervals the chlorine and hydrochloric acid were frozen out with liquid air and the pressure of the residual hydrogen was measured by means of a modified Pirani gage which had only glass exposed to the reaction mixture.[8]

The hydrogen, prepared electrolytically from a potassium hydroxide solution, was passed over hot copper to remove oxygen, then over phosphorus pentoxide, and through a liquid-air trap into the apparatus.

The chlorine was prepared by two different methods. First, it was prepared by

---

[7] Coehn and Jung, Z. *physik. Chem.*, **110**, 705 (1924).

[8] Rollefson, THIS JOURNAL, **51**, 804 (1929).

treating maganesc dioxide with hydrochloric acid and washing the liberated chlorine with water and concentrated sulfuric acid, and then condensing for introduction into the apparatus. The second method was to heat anhydrous cupric chloride. In both cases the chlorine was distilled at least once in a high vacuum and was introduced into the reaction bulb at its own vapor pressure at the melting point of ether or methyl alcohol, depending on the conditions desired, In some experiments the chlorine pressure of Cl_2 was kept constant during the experiment by leaving the reaction chamber connected to the supply of chlorine in the freezing bath. In the other experiments the pressure of hydrogen used was so small compared to the chlorine pressure that the chlorine supply could be sealed off without making the percentage change in the chlorine pressure very large. The vapor pressure of the chlorine at the melting point of ether as interpolated from data in the Landolt-Börnstein "Tabellen" is 1.4 mm. The value at the melting point of methyl alcohol is obtained from Harteck's data[9] as 13.7 mm.

TABLE I

DATA FOR A TYPICAL RUN

Reaction vessel filled with chlorine at vapor pressure at melting point of ether (−116°). Pressure of chlorine, 1.4 mm. Chlorine supply sealed off before experiment. Temperature, 24.8°.

t, min.	Gage reading	Press. of H_2, mm.	Log p	t, min.	Gage reading	Press. of H_2, mm.	Log p
0	1040	0.078	−1.108	256	793	0.0195	−1.710
31	998	.066	−1.180	401	739	.0080	−2.097
106	910	.045	−1.347	461	728	.0055	−2.260
166	855	.032	−1.495	609	712	.0018	−2.745
196	830	.0275	−1.561	692	707	.0007	−3.155
				1400	704	.0000	.....

These results are plotted in Fig. 1. From the straight line obtained for the log p-t plot, we may conclude that there is no change in the rate constant as the pressure of H_2 is diminished. The slight curvature in the region of low pressures can be attributed to a small error in the zero reading of the gage. The value for $d(\log p)/dt$ in this case is —0.144, using the pressure in mm. and time in hours. In ten other experiments, six being with the chlorine reservoir in a freezing bath of melting ether left connected to the reaction vessel, the slope did not vary from this by more than a factor of two.

In order to find the effect of varying the chlorine pressure, runs were made at the two pressures previously mentioned. As the sensitivity of H_2 and Cl_2 is not the same for all mixtures, the reaction vessel was left connected to the source of chlorine and the rate constant determined with the chlorine at the melting point of ether, then at the melting point of methyl alcohol and then again at the melting point of ether using one filling of H_2. The ratio of the rates was found to be about 10 ± 1 in four experiments, which is the same as the ratio of the pressures, so we may conclude that the rate equation at low pressures with excess chlorine remains

$$-\frac{d(H_2)}{dt} = KI_0(Cl_2)\,(H_2)$$

---

[9] Harteck, *Z. physik. Chem.*, **134,** 21 **(1928).**

Theoretical

The results have shown that whether we consider that the active form of chlorine reacts with H_2O, H_2 or Cl_2, this active form must have a life period considerably longer than has been found for any optically excited states. It follows that the chlorine molecule must be dissociated by the light presumably, according to Franck's theory, into a normal atom and one in the $^2P_1$ state. The next stage in the problem is to decide whether one or both of these start the reaction chain and what the first step in this chain is. Since we have no HCl formed by visible light if the gases are carefully dried, we may conclude that water enters into the reaction chain before any HCl is formed. It can have no effect on the initial absorption process since it has been shown by Kornfeld and Steiner[10] that moist and dry chlorine have identical absorption spectra. Assumption of an addition product with water which has too small an absorption to be noted is invalid since the concentration of such a complex, and therefore the reaction rate, should be dependent on the water vapor pressure up to a much higher pressure than the experimentally found 10^{-5} mm. It follows that one or both of the atoms formed by the action of the light must react with water to start the chain process. The most probable type of reaction is the formation of an addition compound, $Cl\cdot H_2O$, since any other reaction such as $Cl + H_2O = HCl + OH$ might be expected to be followed by reactions which would result in oxygen being formed, and there is no evidence for such a step. Furthermore, the nature of the effect of the water-vapor pressure on the reaction rate indicates that it is the chlorine atom

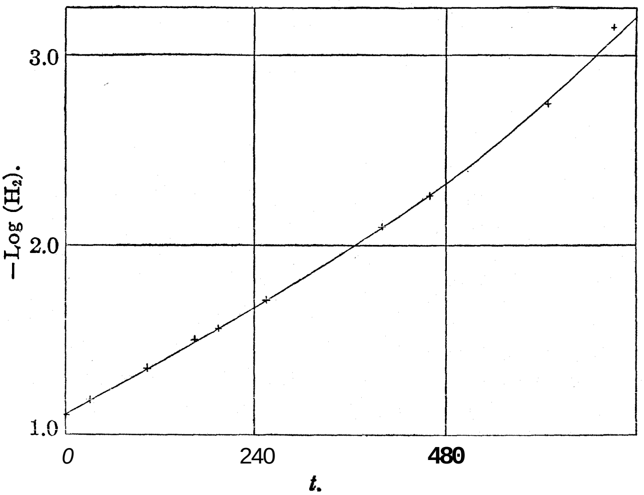


Fig. 1.

---

[10] Kornfeld and Steiner, Z. *Physik*, 45,325 (1927).

in the $^2P_1$ state which reacts. If it were a normal atom which reacted, the rate should depend on the relative number of water molecules and chlorine atoms, which means that under a given set of conditions the rate should be approximately linearly proportional to the water-vapor pressure. On the other hand, if it is the activated atom which reacts, the number remaining in the active state long enough to react with a water molecule falls off exponentially as the water-vapor pressure is decreased. This is in accord with the experiments of Coehn and Jung.[7] Using their data the life period of the metastable state of chlorine may be estimated to be about two hundredths of a second, which is a reasonable value.

Starting in this way we may build up the following series of reactions

$$Cl_2 + h\nu = Cl + Cl(^2P_1) \qquad (1)$$
$$Cl(^2P_1) + H_2O = Cl{\cdot}H_2O \qquad (2)$$
$$Cl{\cdot}H_2O + H_2 = HCl + H_2O + H \qquad (3)$$
$$H + Cl_2 = HCl + Cl(^2P_1) \qquad (4)$$

The chain may be terminated by such reactions as

$$Cl{\cdot}H_2O + Cl = Cl_2 + H_2O \qquad (5)$$
$$Cl(^2P_1) + Cl = Cl_2 + h\nu \qquad (6)$$
$$H + H = H_2 \qquad (7)$$
$$Cl + Cl = Cl_2 \qquad (8)$$
$$H + Cl = HCl \qquad (9)$$

With low hydrogen pressures (5), (6) and (8) will be the limiting reactions, whereas with low chlorine pressures Reaction (7) may play an important role.

The observed reaction rate is determined by the number of reaction chains started and the length of these chains. The number of chains which are started will depend on the number of $Cl(^2P_1)$ atoms formed by the absorption of light which react according to (2) before they lose their activation by collision. In ordinary moist gases (2) is very fast, so that (1) becomes the determining reaction for the number of chains started. For small absorption of light the rate for (1) becomes

$$\left(\frac{d[Cl(^2P_1)]}{dt}\right)_1 = k_1I_0(Cl_2)$$

where k_1 is a constant including such factors as the absorption coefficient and thickness of the absorbing layer. I_0 is the intensity of the incident light.

The other factor in determining the observed reaction rate, the length of the chains, is determined by the preponderance of (3) and (4) over the reactions (5) to (9). In the experiments described in this paper we have found that the reaction rate is proportional to the hydrogen pressure if the chlorine pressure and light intensity are constant. This may be interpreted by saying that the length of the reaction chains is determined by the extent that (3) predominates over (5), as (4) under these conditions is one of the fast reactions of the system. At high hydrogen pressures **(3)** becomes fast and (4) is the rate-determining reaction. From these conditions we obtain the limiting rate laws (1) for excess chlorine

$$\frac{d(HCl)}{dt} = kI_0(Cl_2)(H_2)$$

and (2) for excess hydrogen

$$\frac{d(HCl)}{dt} = kI_0(Cl_2)^2$$

Several writers have attempted to give derivations of these equations based on the mechanisms they have proposed. In these derivations it has been common practice to calculate steady state concentrations of such intermediate substances as chlorine atoms, hydrogen atoms and various active molecules. In view of the fact that we have very little information concerning the factors influencing the existence of such substances in a gas mixture, such calculations require the introduction of so many assumptions that they must be considered extremely approximate. We shall take the stand that it is unnecessary to consider these steady state concentrations, but instead we shall say that each step in the mechanism is to be considered as having a group of side reactions associated with it. If a particular step is one of the rate-determining steps, then these side reactions proceed with a rate comparable with the main reaction. Thus when we have excess chlorine we have said that the rate is determined by the predominance of **(3)** over (5), but there may be other unknown side reactions as well. The net result, however, is such that if we consider the conditions favoring the side reactions involving $Cl{\cdot}H_2O$ as constant, then the relative number of $Cl{\cdot}H_2O$ molecules reacting with H_2 and entering into side reactions is determined by the pressure of H_2.

In the intermediate region the rate equation as given by Thon (omitting the factor due to oxygen) is

$$\frac{d(HCl)}{dt} = \frac{kI_0(Cl_2)(Hz)}{k'(H_2) + k''(Cl_2)}$$

This equation may also be explained on the basis of the proposed mechanism. The numerator of the right-hand member of the above equation has the form given, since the rate depends on the amount of light absorbed and on Reactions **3** and 4. The denominator is due to the fact that the chain-terminating reactions, 7 to 9, require triple collisions in order to dispose of the energy of reaction, and therefore their rates will depend on the total pressure, thus making the rate of formation of HCl inversely proportional to the total pressure, that is, to (Hz) + (Cl_2). Since the hydrogen and chlorine molecules are not equally efficient in removing the reaction energy in these triple collisions, the coefficients of the two terms in this sum will not be identical; hence we find the coefficients k' and k'' in the rate equation. This effect due to the total pressure in the system would ultimately reduce the rate equation to the simple limiting forms which have been given, but is scarcely sufficient to account for these simple forms holding over as wide a range as they do. However, when we introduce the additional condition that **(3)** shall be the principal rate-determining reaction at low hydrogen pressures and (4) at high hydrogen pressures, we see that the two effects aid each other in reducing the rate equation to the simple forms, so that it is to be expected that the more complex form will be required only in a rather narrow range. This range will be determined by the relative values of the rate constants for **(3)** and (4) and the coefficients k and k". Experimentally it has been found to lie between (Hz) $> {}^1/_4(Cl_2)$ and $(H_2) < 2(Cl_2)$, the upper limit being somewhat uncertain.

Another point for discussion is the assumption in (4) that the chlorine atom formed by that reaction is in the $^2P_1$ state. This assumption is not necessarily true, so that formation of a normal chlorine atom in this reaction must be considered as one of the ways of terminating the chain. However, the energy of activation of the chlorine atom is so small that the atom may acquire this activation by collision as the HCl molecule and Cl atom fly apart. Whether the $Cl(^2P_1)$ is formed directly or by collision, the ultimate result may be considered as corresponding to (4).

In comparing the mechanism proposed in this paper with others which have been proposed, it is to be noted that the principal change made is the introduction of water into the reaction chain. This point has already been discussed. With regard to other features of mechanism, an interesting one is the assumption made by Cremer[11] that the reaction chain involves the formation of Cl_3. She disregards the role of water in setting up her mechanism, but otherwise she is able to account for the observed rate equations. The experimental data available are insufficient to decide whether Cl_3 is formed in the chain or not, but some experiments have been planned which it is hoped will throw some light on this point. If such a mechanism should be adopted, water would enter the chain prior to the formation of Cl_3.

One objection which has been raised against the atomic chain mechanism is that all the experiments which have been tried in which the chlorine has been illuminated and then mixed with hydrogen have failed to show the formation of hydrochloric acid, although the time between illumination of the chlorine and its mixing with hydrogen has been less than the life period of the $Cl(^2P_1)$ as calculated in this paper. These experiments have been tried in narrow tubes and under such conditions that it is quite likely that the $Cl(^2P_1)$ atoms are deactivated by collisions with the walls as they are swept through the tube in a much shorter time than would

---

[11] Cremer, *Z. physik. Chem.*, *128*, 285 (1927). See *also* Gohring, *Z. Elektrochem.*, *27*, 511 (1927).

be the case if they were left in the middle of a large volume of gas. Before such experiments can be considered as being definitely against an atomic chain theory, it must be established that chlorine atoms could survive under the experimental conditions used long enough to get mixed with the hydrogen.

So far no account has been taken of the various substances which act as inhibitors for this reaction. The only one which has been studied quantitatively is oxygen, in which case it has been found that the rate of formation of hydrochloric acid is roughly inversely proportional to the pressure of the oxygen. In the proposed mechanism the oxygen could diminish the rate of formation of HCl by removal of the hydrogen atoms or by deactivating the $Cl(^2P_1)$; in other words, it diminishes the length of the chain. The magnitude of this effect is proportional to the oxygen pressure which makes the length of the chains and therefore the rate of the reaction inversely proportional to the oxygen pressure. This proportionality will hold only as long as the oxygen is one of the principal causes for the termination of the reaction chain. At very low oxygen pressures the other factors influencing the length of the chain predominate and the oxygen effect becomes negligible.

Summary

The photosynthesis of hydrochloric acid has been studied at low pressures with excess chlorine and has been found to follow the rate law

$$\frac{d(HCl)}{dt} = kI_0(H_2)(Cl_2)$$

From these experiments and the work of other observers it is concluded that the action of light on this reaction is to form chlorine atoms in the $^2P_1$ state which serve as the starting point for the reaction chain. **A** mechanism is formulated which accounts for the action of water in this system and is in accord with the observed rate equations.

BERKELEY, CALIFORNIA

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

THE HEAT CAPACITIES OF ETHYL AND HEXYL ALCOHOLS FROM 16°K. TO 298°K. AND THE CORRESPONDING ENTROPIES AND FREE ENERGIES

BY KENNETH K. KELLEY[1]

RECEIVED OCTOBER 31, 1928 PUBLISHED MARCH 6, 1929

In an earlier paper low temperature thermal data were given for methyl alcohol.[2] This paper presents similar results for ethyl and hexyl alcohols. The ethyl alcohol has been studied by Gibson, Parks and Latimer[3] and by Parks,[4] whose measurements go down to liquid-air temperature. The measurements here go to liquid-hydrogen temperatures and omit no large temperature intervals between determinations.

The apparatus and methods used have already been described[2] and need not be mentioned here.

Materials

Ethyl Alcohol.—A good grade of ethyl alcohol was allowed to stand on a steam-bath over lime for one week and distilled. It was then put over lime for five days and redistilled. Finally, three fractionations were made, two with lime present and one with metallic calcium. The final product of about 500-cc. volume had a boiling point range of 0.03" and a density, d_4^{25}, 0.78520. This density corresponds to 99.96% ethyl alcohol if the impurity is assumed to be water. The data in the "International Critical Tables"[5] are the basis for this estimate.

Hexyl Alcohol.—The hexyl alcohol was a Kahlbaum product. It was dried with sodium carbonate and with lime and fractionated twice. The middle portion used, 50 cc. in volume, boiled at 157.0–157.1° (760 mm.). Its density was found to be $d_4^{23.7}$, 0.8165.

The Specific Heats

The specific heat values expressed in 15" calories per mole are given in Tables I and II and plotted against the temperature in Figs. 1 and 2.

TABLE I

SPECIFIC HEATS OF ETHYL ALCOHOL

1 mole = 46.05 g.

T. °K.	Cal./mole	T, °K.	Cal./mole	T, °K.	Cal./mole
Crystals		27.05b	3.142	43.50	5.751
18.57b	1.458	27.48a	3.192	46.73	6.368
18.66a	1.456	29.51b	3.565	50.13	6.842
21.40b	1.906	30.43a	3.632	54.26	7.317
22.00a	1.986	32.81b	4.028	58.67	7.777
24.47b	2.586	36.49	4.567	62.62	8.274
24.81a	2.619	40.05	5.098	66.21	8.657

---

[1] National Research Fellow in Chemistry.

[2] Kelley, THIS JOURNAL, 51, 180 (1929).

[3] Gibson, Parks and Latimer, *ibid.*, **42**, 1547 (1920).

[4] Parks, *ibid.*, **47**, 338 (1925).

[5] "International Critical Tables," Vol. III, p. 116.

TABLE I (*Concluded*)

T, °K.	Cal./mole	*T*, °K.	Cal./mole	T, °K.	Cal./mole
68.27	8.896	40.75	5.790	102.87b	19.21
69.92	9.053	44.27	6.451	104.43a	19.23
73.15	9.241	47.82	7.077	104.93b	19.31
77.57	9.527	51.63	7.680	107.99b	19.16
81.71	9.872	55.92	8.196	108.21a	19.26
85.53	10.25	60.14	8.703	**Liquid**	
90.11	10.56	64.28	9.232	163.51	20.74
92.51	10.71	70.76b	9.96	167.90	20.80
96.20	11.01	73.09a	10.21	172.22	20.88
100.06	11.29	75.07b	10.47	176.65	20.95
104.07	11.63	77.28a	10.72	181.23	21.16
108.76	11.91	78.80	10.83	185.57	21.22
113.56	12.28	79.07b	10.92	191.68	21.24
117.68	12.52	81.46a	11.25	192.61	21.26
121.86	12.88	82.82b	11.35	195.98	21.27
125.99	13.08	83.91c	11.49	197.34	21.31
130.18	13.18	85.83a	11.90	208.13	21.77
132.55	13.43	86.75b	12.03	212.94	21.80
Glass		90.11a	12.76	217.64	22.23
18.19	1.830	90.47b	12.73	238.19	22.70
21.00	2.244	93.57b	14.22	260.56	23.77
23.11	2.728	94.09a	15.15	265.48	24.01
25.06	3.188	96.48b	18.40	271.02	24.41
27.19	3.655	97.63a	19.10	277.52	25.00
29.76	4.046	98.66b	19.07	288.95	25.91
33.12	4.542	100.78b	19.14	294.31	26.26
37.00	5.166	100.96a	19.11		

TABLE II

SPECIFIC HEATS OF HEXYL ALCOHOL

1 mole = 102.11 g.

T, °K.	Cal./mole	T, °K.	Cal./mole	T, °K.	Cal./mole
Crystals				**Liquid**	
18.28	1.695	85.38	17.35	229.64	46.75
23.36	2.823	94.59	18.70	240.19	48.06
27.11	3.819	103.26	19.95	250.73	48.81
30.72	4.782	111.54	21.23	260.70	50.00
35.36	6.103	120.31	22.43	270.57	51.77
40.41	7.473	128.66	23.86	280.56	54.78
44.92	8.670	136.78	24.71	290.01	55.56
49.19	9.739	145.82	25.77		
55.82	11.38	154.09	26.85		
60.97	12.68	162.65	27.64		
66.33	13.89	171.69	28.51		
71.01	14.78	180.86	29.77		
76.52	15.80				

Ethyl alcohol may be obtained at low temperatures in either the crystalline or the glassy state. At hydrogen temperatures the curves for glass and crystals are nearly parallel but are converging slightly. At 50°K. the increase in slope of the glass curve over that of the crystals is easily perceptible in the figure. Between 90 and 96°K. the heat capacity of the glass undergoes a rapid increase of over 50%. This phenomenon is typical of heat-capacity curves for glasses and has been previously studied for ethyl alcohol by Gibson, Parks and Latimer[3] and by Parks,[4] for glycerin by Simon[6] and by Gibson and Giauque,[7] and for propyl alcohol and propylene glycol by Parks and Huffman.[8] When the ethyl alcohol glass is warmed to 110°K. crystallization invariably begins. This is similar to the behavior of propyl alcohol glass.[8] For this reason no measurements are given between 110° and the melting point temperature of the crystals. Parks and Huffman[8] found that the shape of the curve in the region of the rapid rise depended upon the previous history of the glass, that is, upon the annealing. Therefore care was taken in this work always to prepare the glass in the same manner. This was done by breaking the vacuum with approximately the same pressure of hydrogen (1 cm. of mercury) each time and then cooling as rapidly as possible to the temperature of liquid air. Two sets of measurements which are in complete agreement

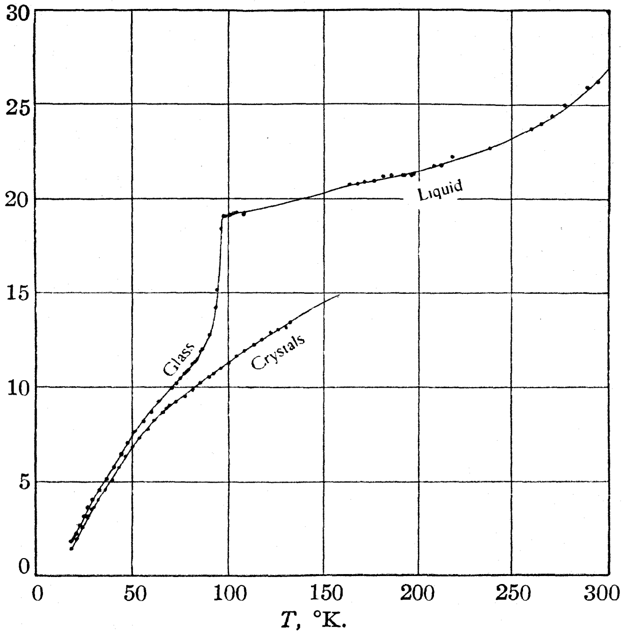


Fig. 1.—Heat capacity of ethyl alcohol in calories per mole.

---

[6] Simon, Ann. *Physik*, [4] 68, 241 (1922).
[7] Gibson and Giauque, This Journal, 45, 93 (1923).
[8] Parks and Huffman, *J. Phys. Chem.*, 31, 1842 (1927).

were made in this region and are distinguished in Table I by "a" and "b." The point marked "c" was obtained just prior to cooling the glass to liquid-hydrogen temperature.

In the region of the rapid rise the thermal conductivity is poor and the corrections for heat interchange with the surroundings are abnormally large due to the long equilibrium period at the end of each determination. However, equilibrium was rapid below **90"** and above **100"**. To test the accuracy obtained in this range a determination was made starting at **86.02"** and ending at **103.14'**. The heat necessary to raise the temperature of the calorimeter and contents through this interval was **273.7** calories,

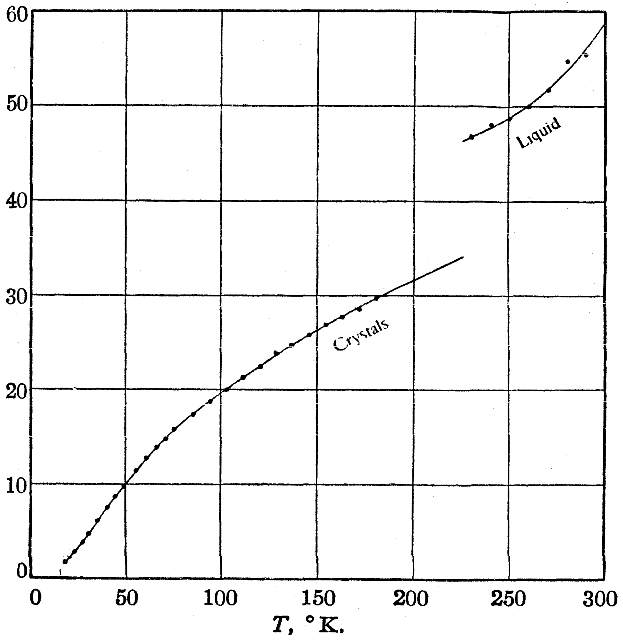


Fig. 2.—Heat capacity of hexyl alcohol in calories per mole.

while the graphical calculation from the C_p *vs.* T plot gave **275.2** calories, a difference of 0.55%. It seems safe to say, therefore, that the accuracy obtained for the glass in this region is about **0.5%** less than that for the crystals.

Two sets of determinations were made on the ethyl alcohol crystals below **35°K.** and are in very good agreement. Above 158.6°K. this alcohol was liquid.

Except for the short interval on the ethyl alcohol glass which has already been discussed, the specific heat measurements have the same accuracy as that given for those on methyl alcohol. That is, "the accuracy of the results depends upon the temperature. Below 20° the error may be of the order of 1% due to the rapid decrease of the dR/dT for the resistance thermometer. Between 20 and 40" the error decreases to about 0.2% and remains such to about 130°. Between 130 and 200" the error increases to about 0.5%. Above 200° certain points may be in error by 1% due primarily to large corrections caused by increased radiation."

The hexyl alcohol was studied in the crystalline and liquid forms only, since it showed no appreciable tendency to form the glass. It melts at 225.S°K. Its specific heat curves are normal in all respects.

The Temperatures and Heats of Fusion

The temperatures and heats of fusion were measured by the methods used by Gibson and Giauque[7] for glycerin. Near the melting point the specific heats of both substances showed considerable increases, which were assumed to be due to premelting caused by small amounts of impurities, and consequently the usual practice of considering the heat involved in excess of the "normal" heat-capacity curves for the crystals as part of the heat of fusion was followed. The mean values in Table III are considered accurate to 0.5%. The result for ethyl alcohol is about 1% higher than the mean of Parks' measurements.

TABLE III

HEATS OF FUSION

Substance	Temp., °K.	Heat of fusion, Cal. per mole 1st result	 2nd result	 3rd result	 Mean
Ethyl alcohol	158.5	1200.8	1200.3	1198.5	1200
Hexyl alcohol	225.8	3679	3672	....	3676

The Entropies

The entropy from 0°K. to the initial temperature of the lowest measurement was obtained by extrapolation using Debye functions with Θ's as

TABLE IV

ENTROPIES

Ethyl Alcohol

0–16°K. (extrap.)	crystals	= 0.45	0–16°K. (extrap.)	glass	= 0.67
16–158.5	crystals	= 16.20	16–158.5	glass + liq.	= 20.94
1200/158.5	fusion	= 7.57	158.5–298.1	liquid	= 14.18
158.5298.1	liquid	= 14.18	$S_{298.1} - S_0$	glass	= **35.8**
			S_0	glass	= 2.6 E. U. per mole

$S_{298.1}$ for one mole of liquid C_2H_5OH = 38.4 ± 0.3 E.U.

Hexyl Alcohol

0–15°K. (extrap.)	crystals	= 0.43
15–225.8	crystals	= 37.82
3676/225.8	fusion	= 16.28
225.8–298.1	liquid	= 14.10

$S_{298.1}$ for one mole of liquid $C_6H_{13}OH$ = 68.6 ± 0.4 E. U.

follows: 109 for ethyl alcohol crystals, 94 for ethyl alcohol glass and 104 for hexyl alcohol crystals. The extrapolated values are small so that this procedure can cause no appreciable errors in the S_{298} values given in Table IV. The entropy between the temperature at the start of the lowest determination and 298.1°K. was obtained in the usual manner.

The value 2.6 E. U. is obtained for the entropy of ethyl alcohol glass at 0°K. Parks[4] obtained 1.79 E. U. but the difference is almost entirely due to the error made in extrapolating from 90 to O°K. by means of the "n" formula of Lewis and Gibson? In the case of the ethyl alcohol crystals this formula causes an error of 3.7 E. U. or 28% in the extrapolated value.

The Free Energies

The free energies of formation of the compounds at 298.1°K. were calculated by means of the fundamental thermodynamic equation, $\Delta F = AH - TAS$.

In obtaining AH for ethyl alcohol the heat of combustion measured by Richards and Davis[10] was used, namely, 7110 Cal. (18°) per g. (in air) at constant volume. This value was corrected to 15° calories, to vacuum weighing and to constant pressure, with 327,340 Cal. per mole as the result. Since this measurement was made at about 291°K. a further correction of −180 Cal. is necessary to correct it to 298.1°K., which gives 327,160 Cal. per mole. For hexyl alcohol the value, 9314 Cal. (15") per g. (in air) at constant volume, obtained by Verkade and Coops[11] was similarly corrected, the result being 951,540 Cal. per mole (measured at 292.6°K.) or 951,200 Cal. per mole at 29S.1°K. These values when combined with the heats of formation of carbon dioxide and water at 298.1°K. which were adopted in previous work[2] give the values of $\Delta H_{298 \cdot 1}$ in Col. 3 of Table V.

The values of $\Delta S_{298 \cdot 1}$ given in the fourth column of Table V are based upon the measured entropies and the values 1.3 units per gram atom for carbon, 29.6 units per mole for hydrogen and 48.9 units per mole for oxygen, the sources of which were also given in the earlier paper. Col. 5 contains the free energies of formation of the compounds at 298.1°K.

TABLE V

THERMAL DATA

The 15° Calorie is used throughout

Substance	Heat of combustion at 298.1°K.	$\Delta H_{298.1}$	$\Delta S_{298.1}$	$\Delta F_{298.1}$
Ethyl alcohol	**327,160**	**−66,340**	**− 77.4**	**−43,300**
Hexyl alcohol	**951,200**	**−92,660**	**−170.8**	**−41,700**

---

[9] Lewis and Gibson, THIS JOURNAL, 39,2554 (1917).

[10] Richards and Davis, *ibid.*, 42, 1599 (1920).

[11] Verkade and Coops, *Rec. trav. ckim.*, 46, 903 (1927).

Discussion

Parks and his co-workers[12] have shown that in an homologous series of normal saturated aliphatic compounds there is an increase in entropy of about nine units per CH_2 group if the substances are considered in the liquid state at 298.1°K., while the free energies of formation from the elements have the same value. The present work bears out these conclusions qualitatively. If the entropy of methyl alcohol, 30.3 * 0.2 E. U. per mole, previously reported[2] is compared with the values in Tables IV, it may be seen that the entropy difference between methyl and ethyl is 8.1 units and between ethyl and hexyl alcohols 30.2 units, or on the average about 7.7 units per CH_2 group. A similar comparison of the free energies shows differences of 700 Cal. between methyl and ethyl and 1600 Cal. between ethyl and hexyl or a change of about 500 Cal. per CH2 group.

The heat of combustion data of Richards and Davis[10] and of Verkade and Coops[11] show a definite increment of about 156,000 Cal. per CH_2 group in the alcohol series from methyl to decyl. The first of these differences is somewhat large and upon this basis Verkade and Coops think that Richards and Davis' value for methyl alcohol is low by 0.1%. If this claim should prove true, the free energy difference between methyl and ethyl alcohols would be reduced to 500 Cal. It is obvious, of course, that if regular differences appear in the consecutive values of any two of these properties (free energies, entropies and heats of combustion) they must appear in the third.

If the free energy difference per CH_2 group found here persists throughout the series, then the higher alcohols are thermodynamically less stable toward the elements than are the lower.

For all practical purposes the author certainly would not hesitate to employ these differences in the calculation of the entropies and free energies of the normal alcohols, propyl, butyl and pentyl.

It is interesting to compare the entropy of ethyl alcohol glass at O°K. reported with the available data for other glasses. Table VI contains these values.

TABLE VI

ENTROPIES OF GLASSES AT O°K.

Quartz glass	Ethyl alcohol	Propyl alcohol	Glycerol
0.9	2.6	3.1 (?)	4.6

The data for quartz glass and glycerol were calculated by Simon and Lange.[13] The value for propyl alcohol is that of Parks and Huffman[12d] corrected as well as possible for the error made in extrapolating below 86 °K.

---

[12] (a) Parks, ref. 4; (b) Parks and Kelley, THIS JOURNAL, 47, 2089 (1925); (c) Parks and Anderson, *ibid.*, 48, 1506 (1926); (d) Parks and Huffman, *ibid.*, 48, **2788** (1926).

[13] Simon and Lange, *Z. Physik,* 38,227 (1926).

It thus appears as would be expected that the entropy of the glass at 0°K. increases with the complexity of the molecule.[14]

Summary

1. The specific heats from 16 to 298°K. of ethyl alcohol crystals, glass and liquid and of hexyl alcohol crystals and liquid have been measured.
2. The heats of fusion and the temperature of fusion have been determined.
3. The entropies and free energies of ethyl and hexyl alcohols at 298° K. and the entropy of ethyl alcohol glass at 0° K. have been calculated.
4. Regularities in the thermal data for the normal saturated aliphatic alcohols have been discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 200]

CATALYTIC EFFECT OF RUTHENIUM SALTS ON THE REDUCTION OF PERCHLORIC ACID BY HYDROBROMIC ACID

BY WILLIAM R. CROWELL, DON M. YOST AND JAMES M. CARTER

RECEIVED NOVEMBER 7, 1928 PUBLISHED MARCH 6, 1929

Introduction

It is well known that both dilute and moderately concentrated solutions of perchloric acid are remarkably unreactive with most reducing agents, although the thermodynamic tendency for the acid to act as an oxidizing agent is undoubtedly very great. Its great power as an oxidizing agent is shown only when the acid is hot and concentrated. Under such conditions the lower valence compounds of osmium and ruthenium are oxidized to the tetroxides.[1] In dilute solutions of perchloric acid the only reducing agents mentioned in the literature as reacting with it are trivalent titanium, trivalent molybdenum and bivalent chromium,[2] the reactions in all three cases being measurably slow. It is to be noted that these three reducing agents have not only a very high reduction potential but have also high reaction rates with most oxidizing agents.

It was found by Dr. Robert H. Dalton in this Laboratory that bromine is evolved on heating mixtures of perchloric and hydrobromic acids containing small amounts of ruthenium chloride, while in the absence of ruthenium no such effect is observed. Subsequent experiments showed that the

[14] See Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 137–138.

[1] Noyes and Bray, "Qualitative Analysis for the Rare Elements," Macmillan Co., New York, 1927, p. 17.

[2] Bredig and Michel, *Z. physik. Chem.*, **100**, 124 (1922).

catalyzed reaction takes place both at room temperature and at 100°, but much more slowly at the lower temperature.

In this paper are described the results of a research on the nature of the catalysis involved in this reaction. We take this opportunity to express our appreciation of the many helpful suggestions made by Professor A. A. Noyes during the investigation. The work was aided by funds granted to him by the Carnegie Institution of Washington.

The resultant reaction under consideration is

$$ClO_4^- + 8Br^- + 8H^+ = Cl^- + 4Br_2 + 4H_2O \quad (1)$$

The fact that eight equivalents of bromine are liberated in the catalyzed reaction per mole of perchlorate ion used up is of importance in discussing the results of rate experiments, since a considerable amount of bromine liberated may correspond to only a small change in the concentration of perchlorate ion.

Interpretation of the mechanism of the reaction involves a knowledge of the chemistry of ruthenium in its numerous oxidation states. Unfortunately this has not been completely investigated. It has been definitely established, however, that bi-, tri- and quadrivalent ruthenium compounds are capable of existing in acid solution. The bivalent compounds form deep blue solutions, which react slowly with atmospheric oxygen to form light yellow or pink solutions that are oxidized by chlorine and bromine, but not by iodine, to the dark orange-red solutions of the quadrivalent salts. The quadrivalent salts in acid solution are quantitatively reduced by iodide[3] or by sulfurous acid to the trivalent state.

The compounds of sexivalent and septivalent ruthenium, the ruthenates (M_2RuO_4) and perruthenates ($MRuO_4$), are rapidly reduced by the halogen acids to the trivalent and quadrivalent states,[4] while with non-reducing acids they are decomposed into the tetroxide and various forms of lower valence.[5]

Ruthenium tetroxide, not only in solution but also in the solid, liquid or gaseous form, is a very active and powerful oxidizing agent. It is not so powerful, however, as permanganic acid, as is shown by the fact that the tetroxide is formed by the action of permanganic acid on the compounds of lower valence. At ordinary temperatures ruthenium tetroxide reacts with hydrobromic acid with the formation of bromine and a mixture of trivalent and quadrivalent ruthenium,[3] the mixture resulting from the fact that trivalent compounds react with bromine to form the quadrivalent compounds.[6]

---

[3] Ruff and Vidic, *Z. anorg. allgem. Chem.*, **136**, 49 (1924).

[4] (a) J. L. Howe, This Journal, 49, 3843 (1927); (b) Krauss and Kükenthal, *Z. anorg. allgem. Chem.*, **136**, 62 (1924).

[5] (a) A. Gutbier, *Z. anorg. allgem. Chem.*, **95**, 183 (1916); (b) F. Krauss, *ibid.*, 132, 301 (1923).

[6] Crowell and Yost, This Journal, 50, 374 (1928).

Preparation of the Solutions

A stock solution of ruthenium chloride was prepared from material purchased as ruthenium trichloride, but containing also some tetrachloride. The solution was made by dissolving the salt in **0.5** *N* hydrochloric acid. The color of this mixture is dark orange-red. A measured portion of the stock solution was treated with chlorine; and, after boiling to expel the excess of chlorine, it was titrated with standard titanous sulfate solution, the end-point being determined electrometrically.[6] The stock solution was found to contain **2.09** g. of ruthenium per liter.

Another ruthenium solution was prepared by treating a definite volume of the stock solution with a small excess of sulfur dioxide, expelling the excess by boiling and adding just enough water to replace that lost by evaporation. The resulting solution had a light orange-red color and it was shown by an electrometric titration with titanous sulfate to contain substantially all of the ruthenium in the trivalent state.

Standard solutions of perchloric acid, hydrobromic acid, potassium iodide and sodium thiosulfate were made up and standardized by the usual well-known methods.

Non-Formation of Bromine from Hydrobromic Acid with Perchloric Acid Alone or with Ruthenium Tetrachloride Alone

To make sure that no bromine is formed by the action of perchloric acid alone on hydrobromic acid or by a reaction between quadrivalent ruthenium and hydrobromic acid, the following experiments were made.

Ten cc. of a mixture which was **0.2905** M in $HClO_4$ and **0.871** M in HBr was heated at 98° in a sealed glass tube for three and one-half hours. The mixture was then diluted three-fold and treated with potassium iodide; no iodine was liberated.

A mixture of **10** cc. of **9** M HBr and **1.00** cc. of **1** M $HClO_4$ was heated for seventy-five minutes in a distilling flask through which a stream of carbon dioxide was passed; after five minutes **0.05** milliequivalent of bromine (due to free bromine originally present in the hydrobromic acid) was found in the receiver by iodimetric analysis, but no more was formed afterward.

A solution which was 8 M in HBr and **0.0246** atomic in ruthenium, present as a mixture of the quadrivalent and trivalent chlorides, was heated in a sealed tube at 98° for one hour, and the resulting mixture was cooled and treated with carbon tetrachloride; no bromine was found to be present.

Effects of Perchloric, Hydrobromic and Hydrochloric Acids and Ruthenium Salt on the Reaction Rate

Experiments were next made to determine the effects of perchloric acid, hydrobromic acid, ruthenium salt and hydrogen ion on the rate of liberation of bromine. In these experiments definite volumes of the reaction mixtures were heated in a water-bath at 98° in sealed glass tubes. The tubes were removed at suitable intervals, broken under solutions of potassium iodide and the liberated iodine was titrated with standard thiosulfate. The stock solution containing both tri- and quadrivalent ruthenium was used, but the iodine liberated by the quadrivalent ruthenium present was so small compared to the total iodine that it could be neglected. The results of typical experiments are shown in Table I. The "bromine formed" is the number of milliequivalents produced per liter.

In Expts. 1 and 2 the composition of the reaction mixtures differed

Table I

Effect of Perchloric Acid, Hydrobromic Acid, Total Acid and Ruthenium Salt on the Reaction Rate

Experiment no.	1	2	3	11	12
Milli-atoms of Ru per liter	2.06	2.06	1.03	1.03	1.03
Molality of HBr	0.5	0.5	0.5	1.0	0.5
Molality of $HClO_4$	.3	.6	.3	0.3	.3
Molality of HCl	.7	.4	.7	.2	2.2
Molality of total acid	1.5	1.5	1.5	1.5	**3.0**
Bromine formed in 15 min	8.9	148	4.5	6.9	6.8
Bromine formed in 30 min	17.3	30.6	8.5	11.1	13.3
Bromine formed in 45 min	23.5	43.1	11.8	15.3	18.5
Bromine formed in 60 min	29.7	54.0	15.7	20.2	24.9
Bromine formed in 75 min	34.8	62.4	20.5	23.7	29.2
Bromine formed in 90 min	41.1	65.8	22.2	25.1	33.5
Bromine formed in 120 min	47.3	76.8	27.3	33.1	43.6
Bromine formed in 150 min	56 5	83.3	32.2	36.0	56.3
Bromine formed in 24 hours	131.9	168.0	100.6	77.4	99.5
Bromine formed in 72 hours	188.9	...	159.7	141.2	178.7

initially only in the concentration of perchlorate, that in Expt. 2 being twice that in Expt. 1. Since the concentration of perchlorate decreased only 2% after two hours, the amounts of bromine liberated within this interval may be compared directly in determining the order of the reaction with respect to the perchlorate. It will be seen that in Expt. 2 the amount of bromine liberated was at first approximately twice that liberated in Expt. 1 in the same interval of time, but that this ratio decreases appreciably as the reaction proceeds. Therefore, at the beginning of the experiments the rate is directly proportional to the concentration of perchlorate.

By comparing in the same way the results of Expts. 1 and 3, the effect of the concentration of ruthenium may be determined. At first the rate of the reaction is directly proportional to the concentration of ruthenium, but as the reaction proceeds, this is no longer true. Thus after twenty-four hours the ratio of the amounts of bromine liberated is 1.3, although the initial ratio of the ruthenium concentrations was 2.0 and that of the perchlorate had decreased by less than 5%.

A comparison of the results of Expt. 3 with those of Expts. 11 and 12 shows that both the bromide and total acid influence the rate appreciably, but in neither case is the rate directly proportional to their concentrations. It is difficult to say whether their action is of a specific nature or is due to activity effects. It is also possible that the total acid and bromide govern to some extent the nature of the complex ions of ruthenium which are present in the solutions and in this way influence the reaction rate.

The Catalytically Active Form of Ruthenium

The fact that the rate does not remain directly proportional to the concentration of perchlorate and of the ruthenium indicates that the catalytically active form of the latter is decreasing in concentration as the reaction proceeds.

If trivalent ruthenium were more active catalytically than the quadrivalent form, the liberation of bromine would decrease the concentration of the former by oxidizing it to the quadrivalent state. The two experiments presented in Table II were made to determine whether this was true. In Expt. 4 the ruthenium was present initially in the trivalent form, while in Expt. 5 it was present in the quadrivalent state. The quadrivalent ruthenium was prepared by treating a definite volume of the stock solution at 98° with a large excess of bromine for forty-eight hours. The excess of bromine was expelled by boiling.

TABLE II

CATALYTIC EFFECTS OF TRIVALENT AND QUADRIVALENT RUTHENIUM

Initial concentrations: ruthenium, 0.00103 atomic; $HClO_4$, 0.3 molal; HBr, 0.5 molal; total acid, 1.5 molal.

Time, min.	Bromine liberated, milli equivalents per liter Expt. 4 Ru^{III}	Expt. 5 Ru^{IV}	Time, min.	Bromine liberated, milli-equivalents per liter Expt. 4 Ru^{III}	Expt. 5 Ru^{IV}
15	22.6	1.08	90	79.8	7.55
30	41.0	2.20	120	88.1	8.65
45	52.i	5.18	150	95.5	9.90
60	62.0	6.28	24 (hours)	154.2	62.10
75	72.1	7.10	72 (hours)	201.5	132.4

The results show definitely that the quadrivalent form is much less active as a catalyst than the trivalent.

Two other types of experiments were made to obtain further evidence regarding the active form of the ruthenium. In the first type the reaction was carried out in a special distilling flask provided with a short reflux condenser bent at an angle with the exit tube and having an inlet tube which could be used to introduce a current of carbon dioxide. The bromine was caught in an acidified potassium iodide solution, which was replaced by a fresh one at measured intervals of time. The liberated iodine was titrated with standard thiosulfate. The results of an experiment of this type and of a similar experiment carried out in sealed glass tubes are given in Table III.

TABLE III

EFFECT OF REMOVAL OF BROMINE ON THE REACTION RATE

Initial concn.: $HClO_4$, 0.3 *N*; HCl, 0.33 *N*; HBr, 1.0 *N*; Ru, 0.00103 at.

Time, hours		0	1	2	3	4	5	6
Bromine lib., milli-equiv. per liter	Dist. expt.	0	51.6	92.2	122.2	147.2	169.5	191.1
	Closed-tube expt.	0	60.7	86.8	103.2	114.5	121.5	130.0

In the distillation experiment the bromine formed was removed fairly rapidly by the stream of carbon dioxide and was thereby prevented from reacting with the trivalent ruthenium to form the less active quadrivalent form, for it is shown later that this reaction is a slow one. The result showed that the rate of formation of bromine is less rapid in the sealed-tube experiments and therefore less rapid with quadrivalent than with trivalent ruthenium.

In the second type of experiments potassium iodide was added to the reaction mixtures and these were heated in sealed tubes. The iodide by its rapid reducing action prevents the formation of much bromine and quadrivalent ruthenium and, consequently, the concentrations of trivalent ruthenium and of bromide are held constant so long as iodide is present. The results of four such experiments are given in Table IV and are shown graphically in Fig. 1. The quantities of iodide added and of bromine formed are expressed in milli-equivalents per liter, both in the table and on the chart.

TABLE IV

EFFECT OF IODIDE ON THE REACTION RATE

	Expt. 4	Expt. 8	Expt. 9	Expt 10
Ru, at. wts. per liter	0.00103	0.00103	0.00103	0.00103
HBr, mole per liter	.5	.5	.5	.5
$HClO_4$, mole per liter	.3	.3	.3	.3
HCl, mole per liter	.7	.7	.7	.7
KI, millimoles per liter	.0	12.0	30.0	60.0
Bromine formed in 15 minutes	22.6	27.5	27.9	29.5
Bromine formed in 30 minutes	41.0	50.6	52.4	55.5
Bromine formed in 45 minutes	52.1	66.6	73.8	79.0
Bromine formed in 60 minutes	62.0	79.2	91.9	99.0
Bromine formed in 75 minutes	72.1	91.0	104.2	118.5
Bromine formed in 90 minutes	79.8	98.5	114.6	132.4
Bromine formed in 120 minutes	88.1	104.0	131.0	158.0
Bromine formed in 150 minutes	95.5	119.7	140.7	173.2
Bromine formed in 24 hours	154.2	192.1	211.6	251.4
Bromine formed in 72 hours	201.5	228.8	258.0	283.0

The curves in Fig. 1 are straight lines and are nearly coincident until the bromine formed equals the iodide added. This shows that the rate of the reaction is maintained practically constant until the iodide is used up. After this point is reached the rate falls off. This is probably due to the oxidation of the trivalent form by the bromine, which begins to accumulate as soon as all of the iodine has been oxidized to iodine.

The results of all of the experiments described in this section show conclusively that the active form of the catalyst is the trivalent ruthenium, and that this active form reacts with the bromine to produce quadrivalent ruthenium, which is much less active catalytically. If, however, bromine reacted very rapidly with the trivalent ruthenium, a much greater decrease in the rate with time would result than was actually observed. It may be inferred, therefore, that trivalent ruthenium and bromine react at a slow but measurable rate to form the quadrivalent ruthenium. To determine whether this was really the case, experiments were carried out as described in the next section.

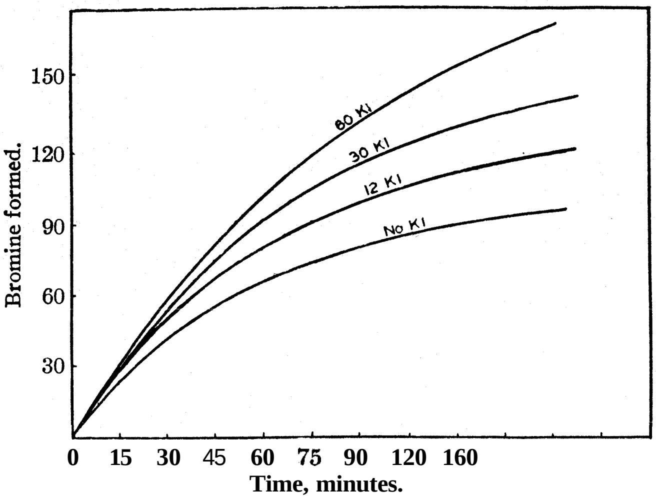


Fig. 1.—Effect of iodide on the reaction rate.

The Rate of the Reaction between Trivalent Ruthenium and Bromine

Stock solutions of bromine water, hydrobromic acid, hydrochloric acid and ruthenium trichloride were mixed and 20-cc. portions sealed in glass tubes. The tubes were placed in a water-bath whose temperature was maintained at 98°. The tubes were removed, one at a time, after measured intervals, cooled rapidly and emptied into a separating funnel. The bromine was extracted with ten 5-cc. portions of carbon tetrachloride. The carbon tetrachloride layer was treated with potassium iodide and the liberated iodine titrated with standard thiosulfate. The results of a typical experiment are shown in Table V.

TABLE V

RATE OF THE REACTION BETWEEN TRIVALENT RUTHENIUM AND BROMINE

Initial concn.: Ru^{III}, 0.00206 *M*; HBr, 0.5 *N*; HCl, 1.0 *N*; Br_2, 0.00850 N

Time	0 min.	30 min.	1 hr.	3 hrs.	5 hrs.	7 hrs.
Br_2 in CCl_4 layer (milliequiv. per l.)	8.5	7.6	7.1	6.8	6.6	6.3

The results, though not very accurate, show that the rate of the reaction between bromine and trivalent ruthenium is slow, as was inferred from the catalytic experiments. It was not practicable to make a complete investigation of this rate, since rather large quantities of ruthenium would have been required.

The Mechanism of the Catalyzed Reaction

Since hydrogen ion and bromide ion exert only secondary effects, the first step determining the rate of the catalyzed reaction might be that expressed by either of the equations

$$ClO_4^- + RuBr_5^{=} + 2H_2O = RuO_4^- + HClO_2 + 5Br^- + 3H^+ \qquad (2)$$

$$ClO_4^- + RuBr_5^{=} + 2H_2O = RuO_4^{=} + 5Br^- + ClO_2 + 4H^+ \qquad (3)$$

Either of these reactions would be in agreement with the experimentally established fact that the rate is directly proportional to the concentration of perchlorate ion and of trivalent ruthenium.

This first slow step might then be followed by the rapid reactions

$$RuO_4^- + 9Br^- + 8H^+ = RuBr_5^{=} + 2Br_2 + 4H_2O \qquad (4)$$

$$RuO_4^{=} + 8Br^- + 8H^+ = RuBr_5^{=} + 1^1/_2Br_2 + 4H_2O \qquad (5)$$

$$HClO_2 + 4Br^- + 3H^+ = Cl^- + 2Br_2 + 2H_2O \qquad (6)$$

$$ClO_2 + 5Br^- + 4H^+ = Cl^- + 2^1/_2Br_2 + 2H_2O \qquad (7)$$

The bromine that is thus formed would then slowly convert the trivalent ruthenium to the quadrivalent state. The fact that ruthenium tetroxide is formed by the action of hot concentrated perchloric acid on trivalent ruthenium compounds is not in disagreement with Reactions 2 and 3, since the ruthenates and perruthenates are decomposed by non-reducing acids into ruthenium tetroxide and ruthenium salts of lower valence. A detailed study of the very slow reaction between perchlorate ion and quadrivalent ruthenium was not made and therefore no data are available for determining its mechanism.

Summary

The reaction $ClO_4^- + 8Br^- + 8H^+ = Cl^- + 4Br_2 + 4H_2O$ is shown to be catalyzed by the presence of ruthenium salts. Its rate is found to be roughly proportional to the concentrations of perchlorate ion and of trivalent ruthenium salt, and to be considerably increased by increasing the concentrations of the bromide and of the acid.

It is shown that the bromine liberated by the reaction slowly converts the trivalent into the quadrivalent form and that removal of the free bromine by a current of carbon dioxide or by addition of an iodide maintains a larger reaction rate. These results, as well as those of comparative experiments in which the ruthenium salt was initially introduced in the trivalent and quadrivalent forms, respectively, show that trivalent ruthenium has a much greater catalytic effect on the reaction than quadrivalent ruthenium.

To explain the observed facts the following mechanism is suggested: the perchloric acid first slowly oxidizes the ruthenium from the trivalent to the sexivalent or septivalent state; the latter is then almost instantaneously reduced by the bromide to the trivalent state. The production of

quadrivalent ruthenium by oxidation of trivalent ruthenium by the liberated bromine accounts for the secondary effect produced by free bromine.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE HEATS OF DILUTION AND SPECIFIC HEATS OF BARIUM AND CALCIUM CHLORIDE SOLUTIONS[1]

BY THEODORE W. RICHARDS AND MALCOLM DOLE

RECEIVED NOVEMBER 8, 1928 PUBLISHED MARCH 6, 1929

Introduction

The recent accurate and systematic investigations of the heats of dilution of various electrolytes carried out by Richards,[2] Lange[3] and their co-workers have been practically entirely limited to uni-univalent salts. The rise of the Debye and Hückel theory of complete dissociation has focused attention, however, on compounds with unsymmetrical valences, because, according to their ideas, the deviations of solutions from those predicted by the perfect gas laws are due partly to the electrical charges on the ions and when these are different the deviations are more marked. Hence a study of the heats of dilution of barium and calcium chloride solutions should prove of particular interest to the modern theories of solutions. Furthermore, one of us[4] had just completed electrochemical and viscosity experiments on barium chloride solutions and was therefore interested in this salt.

Determination of Specific Heats by the Direct Method

Introduction.—As in the previous papers of this series, the procedure in measuring the heats of dilution consisted in diluting a concentrated solution in several successive steps until the experimental errors became greater than the heat effect of the dilution. In addition to observing the rise in temperature of the calorimetric system, in order to calculate the amount of heat energy evolved it was necessary to know the heat capacity of the factors involved. The heat capacity of water and of the apparatus having been determined previously, the only factors remaining unknown were the heat capacities of the salt solutions. If the heat capacity at one

---

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] Theodore W. Richards and Allan Winter Rowe, THIS JOURNAL, 43,770 (1921).

[3] J. Wust and E. Lange, *Z. physik.* Chem., 116,161 (1925); E. Lange and F. Dürr, *ibid.*, 121, 361 (1926); E. Lange and A. Eichler, *ibid.*, 129, 285 (1927); E. Lange and E. Schwarz, *ibid.*, 133, 129 (1928); E. Lange and G. Messner, Z. Elektrochem., 33, 431 (1927).

[4] Grinnell Jones and Malcolm Dole, unpublished results.

concentration is known, then the heat capacities of all the other concentrations may be found by performing the heat of dilution experiments at two temperatures and then calculating the change of the heat capacities of the factors by means of the Person–Kirchhoff equation. To find the heat capacity of the initial solution, a direct method must be used.

Review of **Previous** Values.—Specific heats of barium and calcium chloride have previously been measured by Thomsen,[5] Marignac[6] and Faasch[7] for barium chloride, and for calcium chloride by Thomsen,[5] Marignac,[6] Koch,[8] Dickinson, Mueller and George[9] and W. S. Tucker.[10] Of the data given by these investigators, Marignac's values would have sufficed for the present calculations since they were carried out at suitable concentrations, but although Richards and Gucker found Marignac to be an exceedingly accurate investigator,[11] it was decided to redetermine these values to a greater accuracy if possible.

The Apparatus.—Previous experimental methods of specific heat determinations have been reviewed recently by Richards and Gucker[11] and need not be considered here.

For this investigation the identical apparatus described by Gucker,[12] and further modified by Richards and Gucker,[13] was fortunately available. Many thanks are due to Dr. Gucker for so kindly lending the apparatus to us and for his interest and help in the carrying out of the experiments.

Materials **and** Solutions.—Commercial "C. P." barium chloride was dissolved, filtered, precipitated in freshly distilled alcohol, centrifuged, then again dissolved in water, recrystallized, centrifuged and dried in an oven at 120°. A spectroscopic test showed it to be free **from** strontium. For this direct determination of the specific heat, the solution used was that obtained by diluting the $BaCl_2 \cdot 50H_2O$ solution to $BaCl_2 \cdot 100H_2O$. It was analyzed gravimetrically and found to be $BaCl_2 \cdot 99.97H_2O$.

The calcium chloride was prepared by dissolving calcium nitrate in water, filtering, then precipitating the calcium as the carbonate, dissolving this in freshly distilled hydrochloric acid and finally recrystallizing from water, followed by drying in a centrifuge. A solution made up in the same way as the barium chloride solution proved to have the composition corresponding to $CaCl_2 \cdot 100.13H_2O$. All weighings throughout this paper were referred to the vacuum standard.

Experimental Procedure.—The experimental procedure was practically identical with that described by Gucker,[12] except that not so good

---

[5] Thomsen, "Systematische Durchfuhrung thermochemische Untersuchung," Stuttgart, pp. 110–115.

[6] Marignac, "Oeuvres completes," Vol. II, pp. 624628.

[7] Faasch, "Dissertation," Rostock, 1911, p. 57.

[8] W. Koch, Landolt-Börnstein, "Tabellen," 5th ed., 1923, p. 1262.

[9] H. C. Dickinson, E. F. Mueller and E. B. George, "Bull. Bureau of Standards," Vol. 6, p. 379.

[10] Wm. S. Tucker, *Phil. Trans. Roy. Soc.*, **215A,** 319 (1925).

[11] Theodore W. Richards and F. T. Gucker, THIS JOURNAL, 47, 1892 (1925).

[12] Frank T. Gucker, *ibid.,* 50, 1005 (1928).

[13] Theodore W. Richards and F. T. Gucker, ibid., 51, 712 (1929).

working conditions as he experienced can be claimed here. In his paper[14] he states that the two calorimeters never differed in temperature by more than 0.005° during the heating period. In the present investigation they differed greatly while being heated, probably by as much as 0.1°. The cause of this disconcerting inequality was different lags in the heating coils or in the calorimeters themselves which resulted, as far as could be told, from their being covered with spun gold. The standardization of the apparatus with water reduced this error appreciably; nevertheless, it must be admitted that the difficulty was present.[15] Separate check experiments showed the error of the procedure to be about 0.02% but, due to the uncertainties involved, the results might well be incorrect by as much as 0.05 or 0.1%.

Experimental Results.—In the actual procedure the temperature trends of the calorimeters before and after the heating period were plotted in order to insure that the trend had become constant before the reading was taken. Otherwise than this, the method was identical with that of Dr. Gucker. The experiments were carried out at two temperatures, from 19–21° and from 24–26°. The water standardization gave the same galvanometer deflections at both temperatures, but the barium and calcium chloride solutions were different. The results are summarized in the following tables.

Discussion of the Results.—From the viewpoint of F. Zwicky's theory,[12] the results are interesting because there is a decided increase in

TABLE I

WATER STANDARDIZATION DATA AT 20 AND 25°

Expt.	Av. temp. of heating period, °C.	Wt. of water *in vacuo*, g.	Galv. defl., cm.	Av. defl.
3	20.37, 25.01	245.26	9.00, 8.94	
4	20.12, 25.20	245.66	3.57, 3.57	3.57[a]
5	20.05, 25.01	245.26	8.52, 7.93	
6	19.67, 25.01	246.26	–4.20, –4.31	
12	20.01		–4.62	–4.38[b]
13	21.69	245.26	7.04	8.29[c]

[a] This value, which is intermediate between the two others, falls very near to a straight line drawn between the two other values when they all are plotted on a graph.

[b] The value –4.38 is the average of Expts. 6 and 12.

[c] The value 8.29 is the average of Expts. 3, 5 and 13. The total deflection due to one gram of water was taken as 12.67 cm. Expts. 12 and 13 were performed after the experiments on the salt solutions and constitute, therefore, a check on the constancy of the apparatus.

---

[14] Ref. 12, p. 1013.

[15] Inasmuch as this particular research, which was the last of the experiments here described, had to be carried out in the short time of twelve days (the only time the machine was available before the summer vacation), it was not possible to attempt to overcome this difficulty.

TABLE II

SUMMARY OF RESULTS

Specific heat referred to water over the same temperature range

Expt.	Av. temp. of heating period, °C.	Wt. soln. *in vacuo*, g.	Galv. defl.	Wt. H_2O giving same galv. defl.	Sp. ht.
$BaCl_2 \cdot 99.97H_2O$					
7	20.00	282.47	0.74	245.86	0.87039
	25.00		−5.29	246.37	.87206
8	20.02		0.05	245.91	.87057
	25.00		−5.52	246.35	.87212
$CaCl_2 \cdot 100.13H_2O$					
10	19.87	268.02	6.54	245.41	.91564
					(corrected to 20° C.)
	25.00		1.04	245.83	.91721
11	20.00		5.95	245.44	.91575
	25.00		0.56	245.87	.91736
Averaged values for $BaCl_2 \cdot 99.97H_2O$					
	20.00				.8705
	25.00				.8721
Averaged values for $CaCl_2 \cdot 100.13H_2O$					
	20.00				.9157
	25.00				.9173

specific heat between 20 and 25°. This shows that the change of specific heat with temperature is quite noticeable and that it is a field of research which needs further development.

Heats of Dilution and Specific Heats

Review of Previous Investigations.—Heats of dilution of barium chloride have been measured by Magie,[16] Pratt,[17] and Smith, Stearn and Schneider.[18] The first two workers measured the temperature change only to 0.001° and obtained results which agree only in sign with those of this paper, while Smith, Stearn and Schneider determined the differential heat of dilution, in concentrated solutions only, by adding smaller and smaller amounts of water to a definite amount of solution and then extrapolating to zero amount of water added. The differential heats of dilution are not comparable to the total heats of dilution with which we are concerned in this research.

In addition to these heats of *dilution* might be mentioned the interesting work on the heats of *solution* of barium chloride in water by Lehtonen,[19]

---

[16] W. F. Magie, Phys. Rev,, **35**, 265 (1912).

[17] F. R. Pratt, *J. Franklin Inst.*, **185**, 663 (1918).

[18] G. McP. Smith, Allen E. Stearn and R. F. Schneider, THIS JOURNAL, 42, 32 (1920).

[19] Lyyli Lehtonen, *Soc. Sci. Fennica Comm. Phys.-Math.*, 1, No. 13 (1923).

and in water and mixtures of ethyl alcohol and water carried out by de Kolossowsky.[20]

The differential heats of dilution of calcium chloride solutions have been measured by W. S. Tucker[10] at 18°, and by Harrison and Perman[21] at 40, 50, 60, 70 and 80°. In neither research were smaller temperature changes than 0.001° measured, nor were measurements made in the range of low concentrations. Nernst and Orthmann[22] made one preliminary determination of the heat developed in the dilution of a moderately dilute solution of calcium chloride chiefly for the purpose of comparison with calcium nitrate, which at that concentration has a negative heat of dilution in contrast to calcium chloride, which has a positive heat of dilution. They were apparently solely interested in investigating the validity of the Debye and Huckel theory.

The Experimental Procedure.—The Richards adiabatic calorimeter method was used in this investigation for measuring the heats of dilution. The apparatus and the procedure have already been described in great detail by Richards and Rowe[23] and have been modified further by Richards and Gucker,[24] and improved by Richards, Mair and Hall.[25] The only variation of the procedure introduced in this investigation was to plot the temperature drifts of the calorimeter system before and after the solution and the water were mixed. The temperature readings were then made from the plot, thereby basing the final temperatures on several successive readings rather than on two. in this way there is no doubt that the temperature change of the system, in the most favorable cases, could be determined with an error of only 0.00001°. For example, in Fig. 1 are plotted the various temperatures of the system for Expt. 29 on calcium chloride. The total change was 0,00284" and agreed well with the temperature change in Expt. 30, which was 0.00285°. Needless to say, not all the experiments turned out as well as these two.

Experimental Results.—The method of calculating the results from the rise in temperature was practically the same as in the previous papers of this series. The temperature changes of the calorimetric system were corrected to 20 or 25° and then averaged before calculating any of the results. Since with two exceptions the heat capacities of the factors were used in the calculations, the temperature of the experiment was taken as the final temperature of the reaction. The two exceptions were the dilutions of $BaCl_2 \cdot 50H_2O$ to $BaCl_2 \cdot 100H_2O$ and $CaCl_2 \cdot 50H_2O$ to $CaCl_2 \cdot 100H_2O$, where the temperature of the reaction had to be the initial temperature

---

[20] Nicolas de Kolossowsky, *J. chim. phys.*, 22, 97 (1925).

[21] W. R. Harrison and W. P. Perman, *Trans. Faraday Soc.*, 23, 1 (1927).

[22] W. Nernst and W. Orthmann, *Sitzb. Preuss. Akad. Wis.*, 1926, 51.

[23] Theodore W. Richards and Allan W. Rowe, THIS JOURNAL, 42, 1621 (1920).

[24] Theodore W. Richards and F. T. Gucker, *ibid.*, 51, 712 (1929).

[25] Theodore W. Richards, B. J. Mair and L. P. Hall, *ibid.*, 51, 727 (1929).

because the heat capacities of the products were the data from which the heat capacities of the factors had to be calculated.

The specific heats are the specific heats referred ta water over the same temperature range. They were calculated at **20** and 25° by using the value for the concentrated solution at 20° throughout **the** Person–Kirchhoff equation and the value at 25° throughout the equation. Heat capacities in mayers (joules per degree) at **20°** were found by multiplying the specific heat by 4.1805,[26] and at 25° by multiplying the specific heat by 4.1780.[26] For calculating the heats of dilution at **20** and 25° the average specific heat

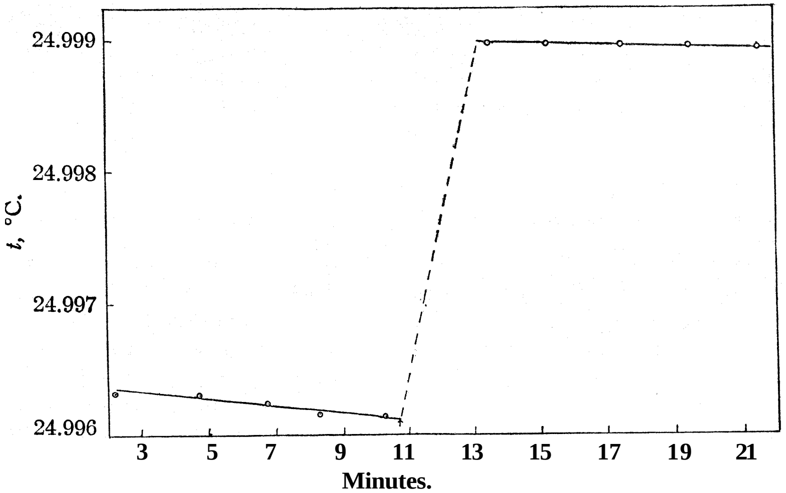


Fig. 1.—Temperature trends of system in Expt. 29 on calcium chloride.

TABLE III

SPECIFIC HEATS

Referred to water over the same temperature range

Concn. moles water per mole of salt	20°	22.5°	25°	Concn. moles water per mole of salt	20°	22.5°	25°
	Barium Chloride				Calcium Chloride		
50	0.7760	0.7775	0.7789	50	0.8487	0.8502	0.8516
100	.8705	.8713	.8721	100	.9156	.9164	.9172
200	.9298	.9303	.9307	200	.9553	.9557	.9561
200.3	.9299	.9304	.9308	400	.9768	.9770	.9772
390.2	.9625	.9627	.9629	800	.9881	.9882	.9883
400	.9635	.9637	.9639	1600	.9939	.9940	.9941
800	.9812	.9813	.9814	3200	.9969	.9969	.9970
1600	.9904	.9905	.9906				
3200	.9952	.9952	.9953				
6400	.9976	.9976	.9976				

---

[26] The heat capacities in mayers of water. See Theodore W. Richards and F. T. Gucker, THIS JOURNAL, 47, 1890 (1925).

TABLE IV

HEAT CAPACITIES IN MAYERS

Concn. in moles H_2O per mole of salt	$BaCl_2$ 20°	$BaCl_2$ 25°	$CaCl_2$ 20°	$CaCl_2$ 25°
50	3.2440	3.2542	3.5480	3.5580
100	3.6391	3.6436	3.8277	3.8321
200	3.8873	3.8885	3.9936	3.9946
400	4.0279	4.0272	4.0835	4.0827
800	4.1019	4.1003	4.1308	4.1291
1600	4.1404	4.1387	4.1550	4.1534
3200	4.1604	4.1584	4.1675	4.1655
6400	4.1705	4.1680		

TABLE V

MOLAL HEATS OF DILUTION AND LOSS IN MOLAL HEAT CAPACITY ON DILUTION

Dilution in moles H_2O per mole salt	Heat of dilution (joules) at 20°	25°	Loss in heat capacity, mayers	Dilution in moles H_2O per mole salt	Heat of dilution (joules) at 20°	25°	Loss in heat capacity. mayers
Barium Chloride				Calcium Chloride			
50- 100	−145.0	90.7	− 47.1	50- 100	638.4	808.7	−34.1
100- 200	75.2	225.3	− 30	100-200	467.9,	579.4	−22.3
200- 400	210.9	305.7	− 16.3	200-400	397.9	470.1	−14.4
400- 800	269.4	333.5	− 13.4	400- 800	358.2	409.9	−10.3
800- 1600	281.9	324.7	− 8.6	800-1600	302.7	347.8	− 9.0
1600- 3200	244.3	285.9	− 8.3	1600-3200	....	276.1	....
3200- 6400	.....	259.1	.....	3200-6400	....	215.1	....
6400-12800	.....	107	.....				
				50- 200	1106	1388	−56 4
50- 200	− 69.8	316.0	− 77.1	50- 400	1504	1858	−70.8
50- 400	141.1	621.7	− 93.4	50- 800	1862	2268	−81.1
50- 800	410.5	955.2	−106.8	50-1600	2165	2616	−90.1
50- 1600	692.4	1279.9	−115.4	50-3200	....	2892	....
50- 3200	934	1566	−124	50-6400	....	3107	....
50- 6400	.....	1825	.....				
50-12800	.....	1932	.....				

over that range was used, since this involves no appreciable error. A negative sign for the heats of dilution means heat absorbed. The absolute value of the final temperature is the same as in the previous papers of this series (that is, the investigations which used the heat of dilution apparatus). The heat capacity of the apparatus devoid of water or solution was 76.4 mayers.

In all of the tables, a correction of −0.05° should be applied to all of the temperature readings. The absolute temperature is then correct to within ±0.02°.

Comparison with Earlier Data

In Table VI the data obtained in this research are tabulated with all other comparable values which are available in the literature. It might be mentioned that Pratt[17] published his values of the heats of dilution for barium chloride only in the form of a graph, which makes it impossible to obtain accurate values for comparison, In the specific heat column, (M.) stands for Marignac[6] and (T.) for Thomsen.[7]

TABLE VI

COMPARISON WITH EARLIER VALUES. SPECIFIC HEATS

Concn.	t, °C.	Sp ht.	t, °C.	Richards and Dole Sp. ht.	t, °C.	Sp ht.
		Barium Chloride				
$50H_2O$	24.5	0.7799 (M.)	20	0.7760	25	0.7789
$100H_2O$	24.5	.8751 (M.)	20	.8705	25	.8721
$200H_2O$	24 5	.9319 (M.)	20	.9298	25	.9307
	18	932 (T.)				
		Calcium Chloride				
$50H_2O$	22.5	0 8510 (M.)	20	0 8487	25	0 8516
$100H_2O$	22.5	.9154 (M.)	20	,9156	25	,9172
$200H_2O$	22.5	.9554 (M.)	20	.9553	25	.9561
	18	.957 (T.)				

HEATS OR DILUTION IN JOULES

Barium Chloride

	Magie[16]		Richards and Dole	
Dilution	t, °C.	Ht. of diln.	t, °C.	Ht. of diln.
50–100	24.5	29.5	25.0	90.7
100–200	24.5	80	25.0	225.3
200–400	24.5	100	25.0	305.7
400–800	24.5	146	25.0	333.5

Discussion of the Results

Although this is chiefly an experimental paper, it would not be amiss to draw a few conclusions from the results. In their investigation of the differential heats of dilution of barium chloride, Smith, Stearn and Schneider[18] made several measurements in the region of concentrated solutions, where the thermal effect on the addition of water is always negative. From this they concluded that the heats of dilution of barium chloride were always negative and so drew the curve on their graph. They also investigated strontium chloride, which they found to have just the opposite heat effect from barium chloride, *i. e.*, the differential heats of dilution were always positive. In both curves they found a sudden change in the region of 1.25 molal; they concluded from this that at that concentration the solutions of 1.25 molal strontium and barium chloride consisted chiefly of the intermediate ions $BaCl^+$ and $SrCl^+$. They explained the difference in the signs of the heats of dilution by the remarkable statement that the heat of hydration must be endothermic in one case and exothermic in the other.

In the light of modern theories of solutions, it is hardly necessary to explain the results in this way. In the first place, if there are complex ions, they are certainly not of the type $BaCl^+$, because the transference number of the barium ion in barium chloride solutions decreases with increasing concentrations, whereas if ions like $BaCl^+$ were present, the transference number would have to increase.[4] The complex ions, then, must be of the type $BaCl_3^-$ or $BaCl_4^{--}$ if they are present at all.

If we consider the very dilute solutions, we find excellent qualitative agreement with the Debye and Hückel theory. Both calcium and barium chloride have positive heats of dilution at very small concentrations, which the theory predicts.[27] The magnitudes of the thermal effects approach each other closely in dilute solutions, as would be expected from the complete dissociation theory. Hence in dilute solutions there is no need of assuming complex ions. Furthermore, in concentrated solutions there are so many effects such as heat of hydration, heat of polymerization of the water molecules, etc., that it is unnecessary if not actually unsound to explain any bend in the curve of the heat of dilution by merely *one* effect, such as that of the presence of complex ions. The heats of solution[19] of calcium, strontium and barium chlorides show a regular decrease in magnitude as the atomic weight increases, those for strontium chloride being half-way between those for calcium and barium chlorides; hence the different thermal effects of these solutions may be due to the intrinsic but regular difference in the atoms and not to any peculiarity of complex ions.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this program of research.

Summary

1. The specific heats of a concentrated solution of calcium and barium chloride have been measured directly.

2. By the indirect method the specific heats and heat capacities of all the solutions have been determined.

3. The heats of dilution and the loss in heat capacity on dilution have been calculated from the observations.

4. Qualitative agreement with the Debye and Hückel theory has been found in dilute solutions.

NEW YORK, N. Y.

---

[27] N. Bjerrum, *Z. physik. Chem.*, **119**, 45 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. V. REACTION WITH FURFURAL

BY R. E. MEINTS AND J. A. WILKINSON

RECEIVED NOVEMBER 9, 1928 PUBLISHED MARCH 6, 1929

Cahours[1] treated furfuramide dissolved in alcohol with hydrogen sulfide gas and obtained a yellow crystalline substance which an analysis indicated was $C_{10}H_4S_2O_2$, thiofurfural. Baumann and Fromm[2] passed gaseous hydrogen sulfide into a solution of furfural dissolved in alcohol, saturated with hydrochloric acid, and isolated a similar body. Quam[3] has shown that furfural is soluble in liquid hydrogen sulfide and reacts with it. An endeavor has been made to prepare the compound mentioned above by the reaction between the two liquids.

The furfural was added to the liquid hydrogen sulfide contained in glass tubes cooled in a bath of solid carbon dioxide and ether. These tubes were then sealed; on coming to room temperature a reaction started and after a few days the whole mass became semi-solid and some yellow crystals formed. The tubes were opened after a week, the excess of hydrogen sulfide was allowed to evaporate and any furfural unacted upon was dissolved out with ether. The residue was soluble in hot ethyl acetate, from which solution yellow monoclinic needles separated. These blackened easily in the air, the black material being insoluble in hydrogen sulfide. When boiled with dilute sodium hydroxide solution the material turned brown but this was soluble in ethyl acetate and the yellow crystals reappeared on evaporating. These crystals softened at 80° and melted between 95 and 98°, which agrees very well with the data for the polymerized material prepared by Baumann and Fromm which softened at SO° and melted from 90–92°. Two samples on analysis were found to contain 28.74 and 28.57% of sulfur, while the theoretical for the compound C_5H_4OS is 28.6%. This indicates that the compound is a monosulfur derivative of furfural.

Furan, furfural alcohol, pyromucic acid, the ethyl ester and the nitroethyl ester of pyromucic acid were all treated in a similar manner but no reaction occurred. Therefore, with furfural it is not the oxygen of the ring that is replaced but the one in the aldehyde group.

Other work in this Laboratory has shown that the aldehydes as a class react with liquid hydrogen sulfide and substitute a sulfur for an oxygen in the aldehyde group, thus liberating water. Since the water is not entirely miscible with liquid hydrogen sulfide, it appears in a separate layer in the tube.

AMES, IOWA

---

[1] Cahours, **Ann.**, **69**, 85 (1845).

[2] Baumann and Fromm, *Ber.*, 24, 3591 (1891).

[3] Quam, THIS JOURNAL, 47, 103 (1925).

NOTE

A Modified Pirani Gage for Use in Corrosive Systems.—In studying reactions in gaseous systems at low pressures, frequent use has been made of the Pirani gage or some modification of it. If one of the gases involved is corrosive or if there is possibility of the reaction rate being affected by catalysis at a metal surface, the ordinary type of gage using a metal wire is unsatisfactory. In this Laboratory these difficulties have been eliminated by using a thin-walled glass capillary filled with mercury as the hot filament. The capillaries are drawn from ordinary 6-mm. Pyrex glass tubing and are usually made about 20 cm. long. These are then ring-sealed into a tube of about 1 cm. internal diameter. The resistance of such a gage varies from about 10 to 30 ohms depending on the size of the capillary.

The most satisfactory way to use this type of gage is to measure the current necessary to keep the temperature of the mercury thread constant. At low pressures the relation between the pressure and the heating current is linear, but at higher pressures the rate of increase of the current with increasing pressure falls off rapidly. These gages have been used with hydrogen and carbon monoxide and found to be quite satisfactory. The response to changes in pressure is so rapid that it does not cause any delay in taking readings. The maximum pressure readable with these gages varies with the accuracy of the current measurement. Using a milliammeter the practical upper limit is about 2 mm. of mercury, but by using a potentiometer this can be increased to several millimeters,

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

GERHARD K. ROLLEFSON

RECEIVED OCTOBER 29, 1928
PUBLISHED MARCH 6, 1929

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OP HYNSON, WESTCOTT AND DUNNING]

SOME MERCURY DERIVATIVES OF HALOGEN COMPOUNDS OF RESORCINSULFONEPHTHALEIN

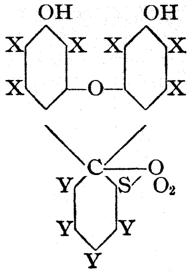
BY FITZGERALD DUNNING AND LARKIN HUNDLEY FARINHOLT

RECEIVED JUNE 14, 1928 PUBLISHED MARCH 6, 1929

For several years this Laboratory has been interested in the preparation of mercury derivatives of phthaleins and sulfonephthaleins and a study of their properties as therapeutic agents. In the course of this research we have had occasion to produce mercury derivatives of halogenated resorcinsulfonephthaleins. As many of the parent resorcinsulfonephthaleins, particularly those with halogen atoms present in the *o*-sulfobenzoic acid residue of the molecule, are unknown, we thought it advisable to make a brief report on the preparation of these compounds.

Results

The compounds which have been prepared may be represented in a general way by the following structural formula



Where X = H, Cl, Br, I, or HgOH and no more than two are halogen or mercury. Y = H, Cl, Br, I; all four being similar in individual compounds.

The following new halogenated resorcinsulfonephthaleins have been prepared: dichlororesorcinsulfonephthalein, resorcintetrachlorosulfonephthalein, resorcintetrabromosulfonephthalein and resorcintetra-iodosulfonephthalein. The mono- and dihydroxymercuri derivatives of all of these compounds have been prepared. In addition, the mono- and dihydroxymercuri derivatives of resorcinsulfonephthalein, dibromoresorcinsulfonephthalein and di-iodoresorcinsulfonephthalein have likewise been prepared.

These sulfonephthaleins show two color changes corresponding to the first formation of the mono- and then the disodium salts. They cannot be used as indicators, however, as they exhibit to a marked degree the phenomenon of dichromatism.

The preparation of resorcinsulfonephthalein has been described in the literature by Remsen and others.[1]

We have made use of the methods described by many of these investigators and with a modification in technique have been able to produce resorcinsulfonephthalein by condensing resorcinol with o-sulfobenzoic acid, o-sulfobenzoic anhydride, the acid ammonium salt of o-sulfobenzoic acid and saccharin. It was discovered that unless the condensation proceeded rapidly, a large amount of a by-product, probably a condensed polymer of resorcinol was formed. This may be separated from the resorcinsulfonephthalein by extraction with alcohol. Very pure resorcinsulfonephthalein can be obtained by any of these methods and, although no attempt was made to crystallize, the material obtained analyzed exactly as predicted by theory.

---

[1] Remsen, *Am.* Chem. J., **6, 180 (1884-1885)**; Remsen and Hayes, ibid., 9, 372 **(1887)**; Remsen and Linn, ibid., **11, 73 (1889)**; Blackshear, ibid., **14, 472 (1892)**; White, ibid., **17, 545 (1895)**; Remsen and McKee, ibid., **18, 802 (1896)**; Sohon, ibid., 20, **257 (1898)**; Fahlberg and Barge, **Ber.,** 22, **754 (1889)**; Sisley, **Bull.** *soc. chim.*, **[3] 17, 822 (1897)**; Orndorff and Vose, THIS JOURNAL, **46, 1896** (1924).

Preparation of Halogenated Resorcinsulfonephthaleins

Dichlororesorcinsulfonephthalein.—Fifty grams of resorcinsulfonephthalein was dissolved in 270 cc. of normal sodium hydroxide, forming the disodium salt, and 200 cc. of water was added. Fifteen grams of sodium chloride and 150 g. of Chloramine T (sodium salt of *p*-toluene chlorosulfonamide) were dissolved in water and added to the first solution. Concentrated hydrochloric acid (approximately 10 cc.) was added to start the reaction. The solution was allowed to stand overnight and a salmon-colored precipitate consisting mainly of *p*-toluene sulfonamide settled out. This mixture was made alkaline with sodium carbonate, to insure the solution of the dye. *p*-Toluene sulfonamide is only slightly soluble in sodium carbonate in the cold; therefore, the solution was cooled to 5–10° for several hours before filtering. The filtrate was acidified with hydrochloric acid and this precipitate was collected on a Büchner funnel. As the precipitate at this point is contaminated with the by-product, it was dissolved in sodium bicarbonate and reprecipitated with hydrochloric acid. This procedure was repeated several times. The final precipitate was collected on a Büchner funnel, washed with a small amount of cold water and then dried at 110°. No attempt was made to crystallize this compound. As obtained it is light red-brown in color, slightly soluble in water, alcohol, acetone and acetic acid. It dissolves readily in dilute sodium hydroxide, forming either a mono- or disodium salt. The solution of the sodium salt exhibits a marked fluorescence; yield, 65%.

Anal. Calcd. for $C_{19}H_{10}O_6Cl_2S$: Cl, 16.23; S, 7.33. Found: Cl, 16.28; S, 7.29.

Dibromoresorcinsulfonephthalein and di-iodoresorcinsulfonephthalein were prepared by the method of Orndorff.[2]

Preparation of Resorcin Halogenated Sulfonephthaleins.—Tetrachloro-, tetrabromo- and tetra-iodo-*o*-sulfobenzoic anhydrides were prepared by Dr. D. Twiss, of this Laboratory. These anhydrides were condensed with resorcinol to form the corresponding phthaleins.

The general method found to be satisfactory for preparing these compounds is as follows. The tetra-halogenated *o*-sulfobenzoic anhydride was mixed thoroughly with resorcinol, in the molecular proportion of 1:2. This mixture was heated in a flask in an oil-bath to 110–120° until the mass became very dark and solid. The temperature must be kept low as otherwise the yields will be poor. This melt was dissolved in 10% sodium hydroxide, the solution filtered and the filtrate precipitated with hydrochloric acid. It is necessary to use concentrated hydrochloric acid to precipitate both resorcintetrachlorosulfonephthalein and resorcintetrabromosulfonephthalein; the precipitates are tarry. These were dried, powdered, washed with hydrochloric acid and then dried. Both compounds are dark brown in color, strong dibasic acids in solution, soluble in water and dilute alkali and moderately soluble in alcohol and acetone. Resorcintetra-iodosulfonephthalein is not a very strong acid and may be precipitated with dilute hydrochloric acid. It is dark brown in color, slightly soluble in water, alcohol and acetone and readily soluble in dilute alkali. The yields were poor with resorcintetrachloro- and tetrabromosulfonephthalein. Resorcintetra-iodosulfonephthalein gave a yield of 80%.

Anal. Calcd. for $C_{19}H_8O_6Cl_4S$: Cl, 28.03; S, 6.34. Found: Cl, 28.24; S, 6.40. Calcd. for $C_{19}H_8O_6Br_4S$: Br, 46.75; S, 4.70. Found: Br, 46.18; S, 4.80. Calcd. for $C_{19}O_8O_6I_4S$: I, 58.23; S, 3.69. Found: I, 58.35; S, 3.70.

Preparation of Mercury Derivatives.—The mono- and di-mercury

---

[2] Orndorff and Vose, THIS JOURNAL, **46**, 1910 (1924).

derivatives of these halogenated resorcinsulfonephthaleins can be prepared by several of the known methods of mercuration.

A solution of molecular proportions of the disodium salt of a sulfonephthalein and of mercuric acetate will react readily on heating. No precipitate is formed by this reaction. The solution is filtered and then precipitated by dilute hydrochloric acid at 60°, with rapid stirring. This will avoid decomposition by loss of mercury. An alternate method is to boil an aqueous solution of the sodium salt of a sulfonephthalein with mercuric oxide in molecular proportions. This solution is filtered and can be taken to dryness on a water-bath or in vacuum and the sodium salt of the mercury derivative obtained immediately in very pure form.

The mercury compounds prepared were all insoluble in water and organic solvents. Both mono- and disodium salts can be readily formed. The solutions of these sodium salts show only a slight fluorescence, as compared with the parent phthalein.

TABLE I

COMPOUNDS AND ANALYSES

Sulfonephthalein	Formula	Mercury, % Calcd.	Mercury, % Found
Monohydroxymercuriresorcin-	$C_{19}H_{12}O_7SHg$	34.3	34.0
Dihydroxymercuriresorcin-	$C_{19}H_{12}O_8SHg_2$	50.1	50.4
Monohydroxymercuridibromoresorcin-	$C_{19}H_{10}O_7Br_2SHg$	27.0	26.3
Dihydroxymercuridibromoresorcin-	$C_{19}H_{10}O_8Br_2SHg_2$	41.8	41.0
Monohydroxymercuridichlororesorcin-	$C_{19}H_{10}O_7Cl_2SHg$	30.7	30.1
Dihydroxymercuridichlororesorcin-	$C_{19}H_{10}O_8Cl_2SHg_2$	46.1	45.8
Monohydroxymercuridi-iodoresorcin-	$C_{19}H_{10}O_7I_2SHg$	23.9	23.8
Dihydroxymercuridi-iodoresorcin-	$C_{19}H_{10}O_8I_2SHg_2$	38.1	37.5
Monohydroxymercuriresorcintetra-iodo-	$C_{19}H_8O_7I_4SHg$	18.	18.0
Dihydroxymercuriresorcintetra-iodo-	$C_{19}H_8O_8I_4SHg_2$	30.7	31.8
Monohydroxymercuriresorcintetrachloro-	$C_{19}H_8O_7Cl_4SHg$	27.8	27.3
Dihydroxymercuriresorcintetrachloro-	$C_{19}H_8O_8Cl_4SHg_2$	42.7	42.3
Monohydroxymercuriresorcintetrabromo-	$C_{19}H_8O_7Br_4SHg$	22.3	21.5
Dihydroxymercuriresorcintetrabromo-	$C_{19}H_8O_8Br_4SHg_2$	35.9	34.7

Analytical

Sulfur and the halogens were determined by the Parr bomb oxidation method. Mercury was determined by the ordinary method of decomposing with sulfuric acid and potassium permanganate, reducing manganese dioxide formed with oxalic acid and precipitating the mercury with hydrogen sulfide. However, when both iodine and mercury are present in the compound this method cannot be used to determine the latter, due to the formation of mercury iodide. The method used was devised by Mr. A. E. Stickels of this Laboratory and is as follows.

To a 0.3- to 0.5-g. sample in a Kjeldahl flask is added 25 cc. of concentrated sulfuric acid and the flask is heated until the material is dissolved. Powdered potassium permanganate is slowly added until the compound is entirely decomposed, taking care not to heat too high in order to prevent any mercury from volatilizing. The mixture is cooled, diluted with about 50 cc. of water and decolorized with oxalic acid or ammonium oxalate. It is diluted to about 400 cc. with water and if a precipitate forms it is heated until the precipitate is dissolved. The solution is cooled, 5 g. of potassium nitrite added and it is heated to boiling. About 2 g. of potassium bromide is added, the solution heated again to boiling, cooled and transferred to a separatory funnel. It is shaken out two or three times with chloroform in order to remove the free bromine. About 1 cc. of phenol is added and the shaking out continued with chloroform or carbon tetrachloride until all of the iodine is removed, which is evident when the chloroform has no color. From time to time more phenol may be required. The aqueous solution is filtered, heated to about 80° and the mercury precipitated with hydrogen sulfide. The precipitate is collected on a tared Gooch crucible, washed with alcohol, then carbon disulfide, again with alcohol and dried in an oven for an hour at 110°. The precipitate is weighed as mercuric sulfide.

This method has been used on known organic mercury compounds to which analyzed potassium iodide has been added with excellent results. Different experimenters have checked analyses with less then 0.3% error.

Summary

1. Several new halogen derivatives of resorcinsulfonephthalein have been made.

2. Mercury derivatives of a number of halogen compounds of resorcinsulfonephthalein have been prepared.

3. A satisfactory method for analysis for mercmy in the presence of iodine is included.

4. Work in this field is being continued.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF NORTHWESTERN UNIVERSITY DENTAL SCHOOL]

POLARIZED LIGHT AND COCAINE DECOMPOSITION

BY H. T. DAILEY[1] WITH H. C. BENEDICT

RECEIVED JUNE 15, 1928 PUBLISHED MARCH 6, 1929

Introduction

Macht and Anderson[2] report that polarized light has a selective action on the decomposition of cocaine, digitalis and quinine as measured by their pharmacological effects. Other chemical effects attributed to polarized light have been reported.[3] Semmens and Baly and Semmens[4] have found that polarized light accelerates the hydrolysis of starch by diastase. Macht announced a substantiation of this work.[5] These reports have been ques-

[1] A portion of a thesis submitted to the Faculty of Northwestern University Dental School in partial fulfilment of the requirements for the degree of Master of Science in Dentistry.

[2] Macht and Anderson, THIS JOURNAL, **49**, 2017 (1927).

[3] S. S. Bhatnagar, *Science*, 64, 359 (1927).

[4] Semmens, *Nature*, **cxi**, 49 (1923); *J. Soc. Chem. Ind.*, **xlii**, 716 (1923); Baly and Semmens, *Proc. Roy. Soc. London*, 97, 250 (1924).

[5] Macht, *Proc. Soc. Exptl. Biol. Med.*, **22**, 473 (1924).

tioned by Jones.[6] More recently the carefully controlled experiments of Bunker and Anderson[7] gave reason to doubt the validity of the conclusions of Semmens, Baly or Macht. In a note[8] Macht gave a preliminary report of the effect of polarized light on other alkaloids, all of which are optically active. Macht gives the work a practical turn by reporting that when a bottle of tincture of digitalis is wrapped in thin tissue paper the solution is more decomposed than that in an unwrapped bottle, due to the small amount of polarization of the light by the thin tissue paper.

He suggests as an explanation of this effect[2] that "if 'for every action there is a reaction' we may look at this phenomenon from the other end and argue that if a given solution can turn the plane of polarized light to the right or to the left, then *vice versa* we may expect polarized light also to react on the solution, and tend to produce some rearrangement in its molecules.''

It seemed that an investigation of the effect of polarized light on a substance which did not contain an asymmetric carbon atom would be a test of Macht's theory. Procaine (β-diethylamino-ethyl *p*-aminobenzoate hydrochloride) suggested itself, as it can be tested in much the same way as cocaine. This was also interesting from a practical point of view because procaine is frequently obtained in wrapped bottles or vials.

Before beginning the work on procaine it was considered desirable to attempt the work of Macht and Anderson on cocaine. From this attempt the contrary conclusion is drawn that polarized light does not cause greater decomposition of cocaine solutions than non-polarized light of the same intensity. Experiments in which procaine solutions are irradiated with polarized and non-polarized light of the same intensity do not show any selective effect (unpublished work).

Apparatus

Macht and Anderson[2] used an apparatus in which they obtained polarized light by transmission through a stack of twelve glass plates at the polarizing angle and also with large Nicol prisms, 2.5 and 3.5 cm. in diameter. As we were unable to obtain as large a Nicol prism as this, experiments were tried with a stack of twelve photographic plates (8 in. by 10 in.). These did not give very complete polarization, as tested by a Nicol prism for extinction. It can be computed that 18% of the light transmitted is non-polarized when using twelve plates. Why do Macht and Anderson make careful measurements of the absolute units of energy when they do not indicate how much of this is polarized? An apparatus was therefore built using a plane plate of black Carrara glass (17 by 24 cm.) obtained from Bausch and Lomb. They use this plate in their strain finder for glassware. The plate was adjustable to any angle by a three-point suspension to attain the maximum of polarization. When properly adjusted the center of the plate was completely extinguished by a crossed Nicol prism and the rest

---

[6] Jones, *Ann. Bot.*, 39, 651 (1925).

[7] Bunker and Anderson, *J. Biol. Chem.*, **77**, 473 (1928).

[8] Macht, Science, 66, 653 (1927).

of the plate nearly so. The plate was inside a triangular blackened box (12 by 12 by $13^3/_8$ inches). In the two equal sides of the box six-inch holes were made to take the six-inch stove-pipe used to isolate the light system. In order to obviate any possible changes in the light by absorption in filters, the non-polarized end was balanced as to intensity with the polarized end by increasing its distance from the light source. At the end of each stove-pipe a removable upright was made, having a 0.75-inch hole to allow observation and to take a thermometer and having a shelf to hold the receptacle for the solution.

As a source of light a 400-watt tubular projection lamp rated at 9000 lumens was used. Because its filament lies in one plane, little light is wasted to each side. To diffuse the light a plate of ground glass was placed four inches from each side of the bulb. The intensity of the polarized and non-polarized ends was made the same within 3 or 4% by using a photometer made of two paraffin plates separated by a piece of tin foil. The experimental error of the photometer was determined on an optical bench before calibrating the apparatus. This photometer was placed in the position to be occupied by the receptacle on the polarized side and a 75-watt lamp was adjusted to balance. Holding the distance between the 75-watt lamp and the photometer constant, a position was found on the non-polarized side where a balance was attained. This was made the position of the non-polarized receptacle.

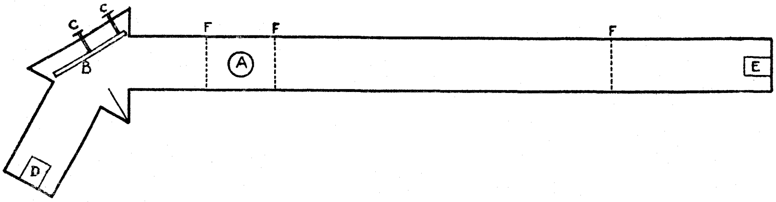


Fig. 1.—Diagram for irradiation device.

A, 400-watt projection lamp; B, black Carrara glass plate; *C*, screws to adjust angle of plate; D, shelf for receptacle on polarized side; E, shelf for receptacle on non-polarized side; *F*, ground plate glass.

The apparatus was so ventilated that the temperatures of the two ends were approximately that of the room, about **23–26**" depending on the day, and were always the same within a half degree throughout an irradiation. Our apparatus was so constructed that the receptacles were about one inch away from the black surface to prevent heating by absorption. From the description of the Macht–Anderson apparatus it seems that the receptacles were placed directly on the blackened surface. Also the distance from the light to the polarized end was less than half the distance to the non-polarized end (see diagram). Therefore, if heating effects came into play, they would be stronger on the polarized side and would if anything enhance the effect he described and which we were unable to obtain.

A few experiments were tried using an "Ahrens" prism of 13 mm. aperture as a polarizing device. The light source was a 15-watt microscope lamp. The heat was absorbed in one experiment by a water cell, in another by a Corning heat-absorbing glass filter.

No attempt was made to have a non-polarized control. The polarized light treated portion was compared with a portion which had been kept in the ice box during the irradiation. As the ice box was dark and cold and the polarized portion was warm (room temperature about **24°**) and light, this gives the greatest chance for the results to agree with those of Macht and Anderson. However, the goldfish anesthesia times are approximately the same (see Table II).

We also made a few tests with the light coming down perpendicularly to the surface of the solution. This is the manner in which many of the experiments of Macht and Anderson were run. It was suggested that we might not be obtaining the results they report because the decomposition was a surface effect, due to some sort of an oriented surface layer on which the polarized light would have a selective effect. The results of our tests do not bear out this suggestion, but may overcome an objection that we did not use the same apparatus as that of Macht and Anderson.

Methods of Testing the Solutions

The two methods used by Macht and Anderson[2] were used by us to determine the extent of decomposition of the cocaine; namely, the goldfish anesthesia time and the growth of *Lupinus albus*. They give no details of either method. We followed the technique given by Adams, Rideal, Rurnett, Jenkins and Dreger[9] on goldfish.

The goldfish were kept in Alberen sinks, the temperature of the water being 20" plus or minus 2". During a test the temperature of the solution was maintained at 20° plus or minus 0.2". Three goldfish were used in each experiment in 250 cc. of solution in a 600-cc. beaker. The time of anesthesia was taken as that given by Adams and co-workers.[9] "When no amount of pressure (on tail or fins) will cause the fish to move." At this point the fish were usually on their sides and had stopped breathing—to all appearances dead. If removed at once, 98% of the fish will entirely recover. Common goldfish about 2 to **3** inches long were used, as supplied by the Auburndale Goldfish Co., Chicago.

Whereas Adams and co-workers[9] found that with alkyl esters of ;b-aminobenzoic acid the goldfish could be used repeatedly after allowing a week for recuperation, we found that they could not be used a second time with cocaine. When the fish were used a week after one exposure no checks could be obtained. The time of anesthesia was longer by five to ten minutes and the individual times seemed to vary more. Fresh distilled water was made and a fresh supply of cocaine was obtained; neither of these changes gave any better results. A fresh supply of goldfish gave us checks and consistent results.

The following test was applied: two goldfish were anesthetized in a 1:5000 cocaine solution in about fourteen minutes. The fish were allowed to recuperate for two hours and again placed in a fresh 1:5000 cocaine solution. They were still swimming normally at the end of an hour. This suggests that unless fresh fish were used throughout, erroneous results might be obtained. It seems that goldfish develop a tolerance for cocaine and unless specially mentioned all the experiments reported were done on fresh fish.

To check our technique with that of Adams and co-workers,[9] tests were made on one of the anesthetics they used at two dilutions. The average

---

[9] Adams, **Rideal, Burnett,** Jenkins and **Dreger,** THIS JOURNAL, 48, **1758 (1926).**

anesthesia time of 8 and 9 fish checked their average time within 0.2 and 0.3 minute.

TESTS ON *n*-BUTYL *p*-AMINOBENZOATE

Concn., M	Time, minutes										Av.	Adams[9] Av.
0.0001	6	6.75	7.75	4.5	5.75	6.75	6.75	7	7	9	6.7	7.0
0.0005	16	16.5	26.5	17.5	23	20.5	21.0	22			20.5	20.7

We are thus reasonably certain that our technique of using the goldfish is essentially the same as theirs.

Another possible error may be introduced by the water used. If doubly distilled water is used, distilled the second time from alkaline permanganate as recommended by Adams and co-workers,[9] much longer times are required for cocaine anesthesia than when ordinary distilled water is used. That this was due to traces of tin from the block tin condenser was shown by boiling some of the doubly distilled water with a piece of cleaned block tin for two hours. A cocaine solution made with this water gave an anesthesia time nearly as short as that of ordinary distilled water and much shorter than the original water. Some of the doubly distilled water was boiled without the tin for two hours; a solution made with this water gave an anesthesia time the same as the original. We hope to look further into this effect.

The results of tests on 108 fish are tabulated in Tables I and II. About 50 more fish were used to obtain an anesthesia time for the non-irradiated solutions. As this time did not appreciably differfrom either the polarized or the non-polarized times for periods of irradiation up to three hours, and as it is not essential to the proposition, it is not necessary to include this data.

We were fortunate in having the assistance of Mr. V. F. Lang of Northwestern University Medical School in running tests on the *Lupinus albus,* as he has been using the method under Dr. C. A. Dragstedt for a year. The solutions were brought to him labeled A, B and C. This assured that the results obtained were not influenced by any preconceived idea of the results expected. The technique employed was that of Macht and Livingston.[10] All of the following steps are carried out in the dark at 20° plus or minus 1°. Seeds of *Lupinus albus* are sprouted in water overnight, and are then placed with the hilum down in moist sphagnum moss for three days. The roots are then measured from a characteristic brown ring to the tip. Seeds with roots of approximately the same length are placed in a series of three-inch test-tubes. The average of ten seedlings is considered a test. A standard is obtained by putting a half and half mixture of Shive's solution,[11] a nutrient solution containing $Ca(NO_3)_2$, $MgSO_4$ and KH_2PO_4 and distilled water

---

[10] Macht and Livingston, *J. Gen. Physiol*, 4, 573 (1922).

[11] Shive, *Physiol Research,* i, 327 (1915).

in the ten test-tubes containing the seeds. The average increase in length in mm. in twenty-four hours is considered 100% growth. The unknown solution is tested by mixing it with an equal volume of Shive's solution, treating ten plants with this mixture and comparing the average growth with that of the standard. Results are reported in percentage of standard growth. The concentrations of cocaine given are those of the original solution. The mixture used to grow the seedlings will thus be half as concentrated.

It should be noted that as the cocaine is decomposed it will have less anesthetic effect and the time of anesthesia for goldfish will be lengthened. On the other hand, as the cocaine has little effect on the growth of *Lupinus albus* and the decomposition products have a great effect,[10] the growth of the plants should be inhibited if there were appreciable decomposition.

In fact it can be computed from the data given by Macht,[10] on the relative growth of *Lupinus albus* in different concentrations of cocaine and its decomposition products, benzoic acid, methyl alcohol and ecgonine hydrochloride that, considering all the lethal effect to be due to the benzoic acid, 17% decomposition of a 1:1000 cocaine solution (0.0029 molar) would completely inhibit the growth and that 1.7% decomposition will give a growth index of 66–67%. Macht[2] finds an index of 75 after the solution has been irradiated for three hours. This would correspond to about 1% decomposition. Yet he obtains a change in the anesthesia time of about 400%.

Experimental Data

In Table I are given the results of the tests on cocaine solutions using the black Carrara glass plate as the polarizing device. Besides the individual times and the average times of anesthesia, the average deviation is included. The percentage increase in time of anesthesia due to the polarized light was obtained by subtracting the average non-polarized time from the average polarized time and dividing by the non-polarized time, results being expressed in percentage. If the non-polarized time is greater than the polarized, the results are negative.

The anesthesia time gradually increases with time of irradiation. This bears out the known fact that cocaine hydrochloride solutions are decomposed by light.

Table II is made up in the same form as Table I. It gives the results of experiments in which the polarized light was perpendicular to the surface of the solution and in which the polarized radiation was obtained by an "Ahrens" prism. In these experiments no non-polarized control was used but the results are compared with a portion of the solution which was kept in the ice box.

In the last experiment if the growth of one seedling which was obviously a "sport" had been omitted from the calculation, the growth index of the

TABLE I

COCAINE HYDROCHLORIDE IN DISTILLED WATER AT 20 ± 0.2°

Concn.	1:5000		1:5000		1:5000		1:5000[a]	
Radiation	1 hour		3 hours		5 hours		6 hours	
	Pol.	Non.	Pol.	Non.	Pol.	Non.	Pol.	Non.
Anesthesia time of individual goldfish	11.0	11.0	15.0	18.0	16.0	15.5	15.0	19.0
	10.7	11.2	14.0	16.0	18.5	18.5	15.0	27.0
	11.2	10.0	13.5	16.5	18.5	18.5	15.0	27.0
	11.5	12.5	11.5	11.5				
	10.7	12.0	12.5	12.0				
	12.5	10.5	13.0	14.5				
			16.0	10.5				
			16.0	12.0				
			18.0	14.0				
Average	11.29	11.2	14.38	13.8	17.6	17.5	15.0	24.1
Av. deviation	0.47	0.70	1.65	2.13	1.13	1.33	0.0	3.43
% increase in time	0.8		3.62		0.57		−37.5	

[a] Old fish.

Concn.	1:5000		1:5000		1:1000		1:1000		1:500	
Radiation	7 hours		12 hours		2 hours		4 hours		3.5 hours	
	Pol.	Non.	Pol.	Non.	Pol.	Non.	Pol.	Non.	Pol.	Non.
Anesthesia time of individual goldfish	19.5	19.5	24.0	29.0	15.7	14.5	6.7	8.5	9.0	9.2
	24.5	25.0	29.0	29.7	15.7	15.7	10.5	9.5	9.5	9.7
	26.0	30.0	34.0	34.0	15.7	15.7	10.5	12.5	10.0	9.7
Average	23.3	24.8	29.0	30.9	15.7	15.3	8.2	10.1	9.5	9.5
Av. deviation	2.56	3.56	3.3	2.0	0.0	0.5	1.7	1.5	0.3	0.2
% increase	−6.0		−6.1		3.2		−9.0		−0.8	

TABLE II

COCAINE HYDROCHLORIDE IN DISTILLED WATER AT 20 ± 0.2° USING VARIOUS METHODS POR OBTAINING POLARIZED LIGHT

Concn.	1:1000[a]		1:500[a]		1:5000[a]		1:5000[a]	
Radiation	4 hours		3 hours		5 hours		6.5 hours	
	Pol.	Non.	Pol.	Non.	Pol.	Non.	Pol.	Non.
Anesthesia time of individual goldfish	G.5	9.2	11.0	7.2	26.5	25.5	30.0	37.0
	10.5	10.5	14.0	11.5	30.0	30.0	35.0	41.0
	10.5, 11.7	11.0	16.0	11.5	38.0	38.0	59.0	65.0
Average	9.8	10.1	13.6	10.0	31.5	31.1	41.0	47.6
Av. deviation	1.3	0.6	1.8	1.8	4.3	4.6	11.8	8.2
% increase	−3.0		36.0		1.3		−13.8	

[a] In all of these tests the polarized light was perpendicular to the surface of the solution.

Concn.	1:1000[a]		1:1000[b]	
Radiation	2.5 hours		3 hours	
	Pol.	Control	Pol.	Control
Anesthesia time of individual goldfish	13.0	12.0	11.0	13.0
	15.2	16.5	12.0	14.5
	16.5	16.5	13.5	29.2
Average	14.9	15.0	12.0	15.5
Av. deviation	1.3	2.0	1.0	5.8
% increase	0.67		−22.6	

[a] Solution in a plane-sided cell, light polarized by an "Ahrens" prism using a 15 watt lamp.

[b] Solution in beaker in same apparatus.

TABLE III

GROWTH OF 120 LUPINUS ALBUS AS REPORTED BY V. F. LANG

Radiation	Pol.	Non.	Normal	Shive's	Concn.
2.5 hours	96	88	104	100	1:1000
10 hours	126	99.9	102	100	1:1000
10 hours	80	90	90	100	1:500

polarized side would have been 86.5% instead of 80%. It has been the experience of Dr. C. A. Dragstedt that variations of 10% or more are frequently obtained and that unless this difference is consistently obtained it is without significance.[12]

Table IV summarizes the results of Tables I and II, giving the average times of each experiment. We have included the average of the averages, regardless of time of irradiation or concentration. If there were a consistently longer time due to the polarized light, this should show up. However, this average shows a slightly longer time for the non-polarized light, and the average percentage increase in time due to the polarized light is −3.48%. These results are probably within the experimental error of the method.

TABLE IV

SUMMARY OF RESULTS

Radiation time	Concn.	Pol.	Non.	% Increase in time due to pol. light, %	Remarks
1	1:5000	11.29	11.2	0.8	
2	1:1000	15.75	15.3	3.2	
2.5	1:1000	14.9	15.0	0.67	Ahrens prism
3	1:5000	14.38	13.8	3.62	
3	1:500	13.6	10.0	36.0	Perpendicular light
3	1:1000	12.0	15.5	−22.6	Ahrens prism
3.5	1:500	9.5	9.58	− 0.8	
4	1:1000	9.2	10.1	− 9.0	
4.0	1:1000	9.8	10.1	− 3.0	Perpendicular light
5.0	1:5000	17.6	17.5	0.57	
6.0	1:5000	15.0	24.1	−37.5	Re-used goldfish
6.5	1:5000	41.0	47.6	−13.8	Perpendicular light
7.0	1:5000	23.3	24.8	− 6.0	
12.0	1:5000	29.0	30.9	− 6.1	
5.0	1:5000	31.5	31.1	1.3	Perpendicular light
Average of av.		17.8	19.1 Total	−52.2	Av. −3.48

It will be noticed that in one or two experiments the solutions irradiated with polarized light have a slightly longer anesthesia time than the specimen treated with non-polarized light. However, these results are not obtained consistently, and as many or more tests are found which would reverse the conclusion.

---

[12] Personal communication.

Summary and Conclusions

1. A study of the relative effect of polarized and non-polarized light on the decomposition of cocaine has been made, in which (a) several concentrations of cocaine hydrochloride were used; (b) two methods of obtaining a polarized radiation were used; (c) the times of irradiation ranged from one to twelve hours; (d) the effect was tested on goldfish and *Lupinus* albus.
2. The conclusion is drawn that polarized radiations have no selective action in the decomposition of cocaine hydrochloride.
3. Cocaine is slowly decomposed by light.
4. Obvious sources of error which we have tried to eliminate are: the variability of individual goldfish, the tolerance that goldfish develop to cocaine and the effect of traces of impurity in the water.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE SYNTHESIS OF CERTAIN ACRIDINE COMPOUNDS

BY KONOMU MATSUMURA

RECEIVED JUNE 22, 1928 PUBLISHED MARCH 6, 1929

In continuation of work on the preparation of certain acridine derivatives for bactericidal examination,' this paper deals with the preparation of the following compounds.

V. 9-Amino-3,6-dimethoxy-acridinium-methyl Chloride

9-Amino derivatives of acridine compounds are now attracting considerable interest in the field of medicine. Of these, Rivanol (2-ethoxy-6,9-diamino-acridine-hydrochloride) is the only product now employed in practice. The compound described here was prepared as a further contribution to the study of this kind of compounds.

Diphenylmethane, prepared from benzyl chloride, benzene and aluminum chloride by Radziewanowski's method,[2] was first converted into 3,6-diamino-acridone (I) by nitration, oxidation, and subsequent reduction by Schopff's[3] and Staedel's[4] methods, respectively, with a little modification. 3,6-Diamino-acridone was then converted into 9-amino-3,6-dimethoxy-acridine (IT) by hydrolysis with 50% sulfuric acid, methylation with dimethyl sulfate, chlorination with phosphorus pentachloride and subsequent amidation with ammonia. 9-Amino-3,6-dimethoxy-acridine on acetylation, treatment with *p*-toluene-methyl-sulfonate, and subsequent hydrolysis with hydrochloric acid, gave 9-amino-3,6-dimethoxy-acridinium-methyl chloride (IV).

---

[1] Matsumura, THIS JOURNAL, 49, 810 (1927).

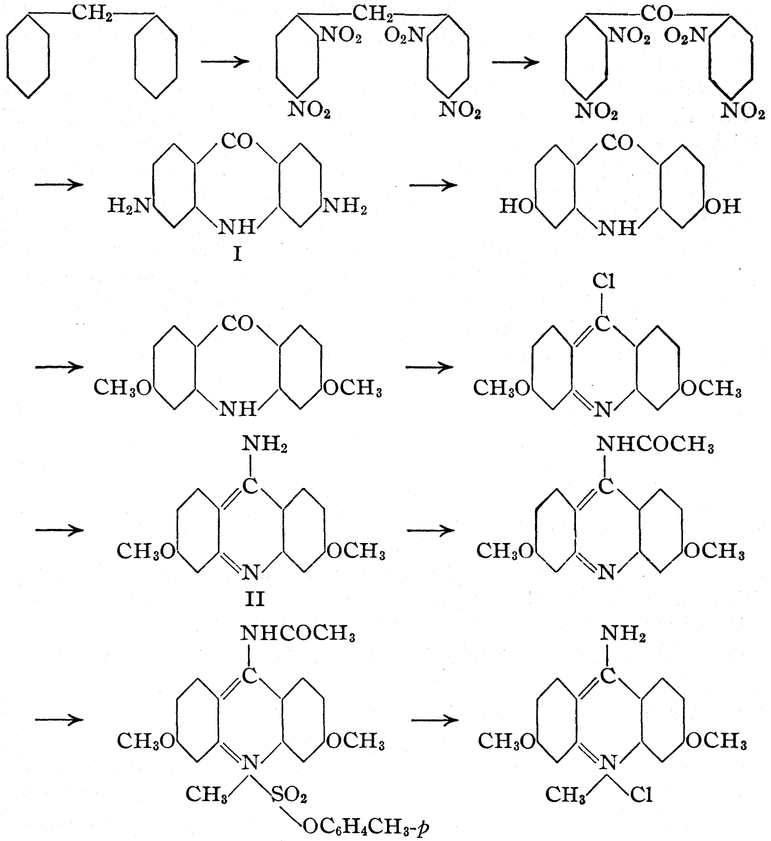
[2] Kadziewanowski, *Ber.*, **28,** 1136 (1895).

[3] M. Schopff, *ibid.,* 27, 2318 (1894).

[4] Staedel, *Ann* , **218,339** (1883)

The methyl iodide of 9-acetamino-3,6-dimethoxy-acridine (III) was obtained by direct combination of the components, but its scanty solubility in water made it disadvantageous in practice for physiological study.

The yields in all these steps of the synthesis are generally good enough for technical operation. The whole process of the synthesis is represented by the following scheme.



Experimental Part

2,4,2′,4′-Tetranitrodiphenylmethane.—The following modification of M. Schöpff's[3] method was used: 135 g. of finely powdered potassium nitrate was dissolved in 700 g. of concd. sulfuric acid below 30° during about three-quarters of an hour. 50 g. of diphenylmethane (b. p 260°) was introduced into the solution under constant stirring during one and one-half hours at 10–25°. The mixture was then gradually warmed to 70° on the sand-bath and kept at that temperature for half an hour under stirring and then allowed to stand. After being cooled, it was poured into 4 liters of ice water, when a light yellow precipitate was obtained which was filtered and washed.

After being dried, it was boiled with 200 cc of alcohol, filtered while hot and re-

crystallized from 400 g. of boiling glacial acetic acid, giving large prisms of light yellow color; m. p. 173°; yield, 81 g. (77%) after recrystallization.

2,4,2',4'-Tetranitrobenzophenone.—For the preparation of this compound by Staedel's method, the following procedure was found to be the best. To the boiling solution of 17 g. of tetranitrodiphenylmethane in 270 g. of glacial acetic acid, 25 g. of chromic oxide was gradually introduced from the upper end of the cooler during half an hour, and kept boiling for two and one-half hours longer.

Next day the separated crystals were filtered from glacial acetic acid, washed with glacial acetic acid, then with water and with alcohol, giving slightly yellowish prisms; m. p. 232°; yield, 16.5 g. (93%). The melting point is not in agreement with Staedel's and Schopff's descriptions (m. p. 225°). The lower melting point may perhaps be due to the presence of unaltered mother substance.

3,6-Diamino-acridone.—An attempt to reduce the nitro derivative to diamino-acridone by tin metal and concd. hydrochloric acid led to the formation of much tar, from which only a small amount of the diamino-acridone could be isolated. It was abandoned then and Schopff's method[3] was used in entirety. This process gave almost colorless needles, which are unaltered at 320'; yield, 10.7 g. (97%) from 18 g. of tetranitrobenzophenone.

3,6-Dihydroxy-acridone.—Attempts to convert the amine into the corresponding hydroxyl compound by the usual method of heating the diazotized solution of the amine led to the formation of much disagreeable black-violet coloring matter, from which only a small amount of dihydroxy-aaidone could be extracted, whereas the direct hydrolysis by sulfuric acid was found very satisfactory.

Twelve g. of 3,6-diamino-acridone, 50 cc. of water and 40 g. of concd. sulfuric acid were heated in an enameled autoclave at 195° for six hours. After being cooled, the contents consisted of a light brown colored cake and a slightly colored liquid. The cake was dissolved in an excess of dilute sodium hydroxide solution and after filtration precipitated again with dilute hydrochloric acid. It was recrystallized from boiling glacial acetic acid or better from boiling alcohol, giving almost colorless thin plates or columns of silky luster. It was unaltered at 320°.

The solution in conc. sulfuric acid gives pure blue fluorescence. It is fairly soluble in hot alcohol, in hot glacial acetic acid and acetone, very difficultly in nitrobenzene and insoluble in water, benzene and ether; yield, 10.2 g. (85%).

Anal. Subs., 0.0940: N_2, 5.2 cc. (16°, 760 mm.). Calcd. for $C_{13}H_9O_3N$: N, 6.17. Found: N, 6.44.

3,6-Dimethoxy-acridone.—To a boiling solution of 9 g. of 3.6-dihydroxy-acridone, 4.6 g. of potassium hydroxide and 5 cc. of water, in 50 cc. of alcohol, 12 cc. of dimethyl sulfate was added from the upper end of the cooler in three separated portions.

A violent reaction occurred at each addition and precipitate was produced. The mixture was boiled for an hour longer. On being cooled, it was made strongly alkaline by the addition of a solution of 4.5 g. of sodium hydroxide in 100 cc. of water. The precipitate of microscopic columns was filtered after standing for one night, washed with water and recrystallized from glacial acetic acid.

It gave almost colorless short needles or plates, unaltered at 320°; its concd. sulfuric acid solution shows a bluish-green fluorescence, and it is fairly soluble in hot alcohol and hot glacial acetic acid, but insoluble in benzene and ether; yield, 7.8 g. (77%).

Anal. Subs., 0.0937: N_2, 4.5 cc. (16°, 759 mm.). Calcd. for $C_{15}H_{13}O_3N$: N, 5.49. Found: N, 5.58.

9-Chloro-3,6-dimethoxy-acridine.—5.1 g. of 3,6-dimethoxy-acridone, 4.6 g. of phosphorus pentachloride and 12 cc. of dry toluene were well mixed into a homogeneous paste. The mixture was gradually warmed to 120–130° during an hour with occasional stirring and kept at that temperature for three hours longer. The toluene and phosphorus oxychloride were driven off by the current of dry air and the material was allowed to cool. The yellow mass thus obtained was treated with ice water, converted into a fine powder, and on making alkaline with dilute aqueous ammonia, free base was obtained; m. p. 152–8°; yield, 5.6 g. The product so obtained is good enough for use in the next step of the synthesis. For the further purification for analytical use, the crude product was dissolved in cold alcohol, and the filtered solution was concentrated in vacuum at room temperature. On addition of cold water to the concd. alcoholic solution, the chlorodimethoxy-acridine separated out as long needles of light yellow color; m. p. 184°. It was easily soluble in alcohol with green fluorescence, difficultly in benzene, almost insoluble in water and the solution in concd. sulfuric acid gave an intense green fluorescence.

Anal. Subs., 0.2833: AgCl, 0.1478. Calcd. for $C_{15}H_{12}O_2NCl$: Cl, 12.98. Found: Cl, 12.88.

The hydrochloride gave yellow needles and is very easily soluble in cold alcohol and rather difficultly in cold water.

9-Amino-3,6-dimethoxy-acridine.—A mixture of 70 cc. of absolute alcohol and 3 g. of copper acetate was strongly cooled by ice and salt and saturated with ammonia (dried through calcium oxide) at 0°. To this solution finely powdered, crude 9-chloro-3,6-dimethoxy-acridine prepared from 5.1 g. of dimethoxy-acridone was added and heated at 140° (24 atm.) in an autoclave for eight hours. After the evaporation of alcohol and excess of ammonia, the residual mass was extracted twice with hot dilute hydrochloric acid and then with hot water. The united hot extracts were made alkaline with dilute aqueous sodium hydroxide, when intensely yellow crystals separated and crystallized as yellow prisms from alcohol; m. p. 268°.

It is fairly soluble in ether, easily in acetone and hot nitrobenzene, sparingly in chloroform, benzene and hot water. The solution in concd. sulfuric acid gives a green fluorescence and on dilution with water a violet-blue fluorescence is shown. The alcoholic solution gives a green fluorescence and on dilution with alcohol a pure blue fluorescence. In dilute hydrochloric acid it is rather difficultly soluble, with violet-blue fluorescence, but is fairly soluble on warming; yield, 3.5 g.

Anal. Subs., 0.0570: CO_2, 0.1486; H_2O, 0.0302. Subs., 0.0796: N_2, 7.3 cc. (11.5°, 760.6 mm.). Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.87; H, 5.51; N, 11.02. Found: C, 71.10; H, 5.89; N. 10.90.

The hydrochloride was obtained on addition of an excess of concd. hydrochloric acid to the hot alcoholic solution of the free base and subsequent cooling. It forms light yellow needles which begin to soften at 310° and melt at 315° (decomp.). It is fairly soluble in cold alcohol, rather difficultly in cold water but fairly soluble in hot.

Anal. Subs., 0.3152: 19.6 cc. $N/10$ NaOH. Calcd. for $C_{15}H_{14}O_2N_2 \cdot 2HCl$: HCl, 22.32. Found: HCl, 22.70.

The picrate forms yellow columns from alcohol, begins to decompose at 273° and sharply melts at 285° with foaming.

Anal. Subs., 0.0735: N_2, 9.0 cc. (13°, 770 mm.). Calcd. for $C_{15}H_{14}O_2N_2 \cdot C_6H_3O_7N_3$: N, 14.49. Found: N, 14.64.

9-Acetamino-3,6-dimethoxy-acridine.—9-Amino-3,6-dimethoxy-acridine and some excess of acetic anhydride, under the addition of sodium acetate, were kept for two hours at 100°. The reaction mixture was poured into water and warmed on the water-bath until completely dissolved. On treating the filtered liquid with aqueous sodium carbonate, the acetyl compound is precipitated as light yellow shining needles from alcohol; m. p. 277–278°.

Anal. Subs., 0.0836: 6.7 cc. (12°, 764 mm.). Calcd. for $C_{17}H_{16}O_3N_2$: N, 9.46. Found: N, 9.55.

9-Acetamino-3,6-dimethoxy-acridinium Methyl Iodide.—1.7 g. of 9-acetamino-3,6-dimethoxy-acridine, 5 cc. of methyl alcohol and 1 g. of methyl iodide were heated at 110° for one and one-half hours in a sealed tube. After evaporating the reaction mixture almost to dryness, the yellow mass was treated with boiling alcohol and filtered cold. It forms yellow plates, very sparingly soluble in hot water with blue fluorescence, and also in boiling alcohol; m. p. 310° (decomp.); the yield was the theoretical.

Anal. Subs., 0.2919: AgI, 0.1575. Calcd. for $C_{18}H_{19}O_3N_2I$: I, 29.00. Found: I, 29.15.

9-Acetamino-3,6- diiethoxy **-acridinium** Methyl-*p*-**toluenesulfonate.**—7.1 g. of 9-acetamino-3,6-dimethoxy-acridine was dissolved in 70 cc. of boiling nitrobenzene; 5 g. of p-toluene-methyl-sulfonatewas added to the solution at a time and allowed to cool. The separated mass was filtered, washed with benzene and then treated with boiling benzene. The benzene-insoluble matter was collected and washed with ether. It formed light yellow needles which began to soften at 250° and melted at 280°. It is fairly soluble in hot water, with blue fluorescence, easily in alcohol and fairly soluble in nitrobenzene; yield, 4.8 g.

Anal. Subs., 0.0859: N_2, 4.5 cc. (12.5°, 768 mm.). Calcd. for $C_{25}H_{26}O_6N_2S$: N, 5.81. Found: N, 6.26.

9-Amino-3,6-dimethoxy-acridinium Methyl Chloride.—A mixture of 4.2 g. of the acetaminodimethoxy-acridinium methyl toluenesulfonate, 15 cc. of water and 30 cc. of concd. hydrochloric acid was boiled for eight hours. After cooling, the separated crystals were filtered off and washed with a little water.

It forms yellow needles, unaltered at 315°, fairly soluble in cold water, with intense blue fluorescence, easily soluble in hot alcohol with violet-blue fluorescence, and concd. sulfuric acid solution gives a weak green fluorescence; yield, 2.7 g.

Anal. Subs., 0.0741: N_2, 5.6 cc. (15°, 766 mm.). Subs., 0.3439: AgCl, 0.1604. Calcd. for $C_{16}H_{17}O_2N_2Cl$: N, 9.20; Cl, 11.66. Found: N, 8.91; Cl, 11.53.

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

The following compounds connected with the acridine syntheses have been characterized: 3,6-dihydroxy-acridone, 3,6-dimethoxy-acridone, 9-chloro-3,6-dimethoxy-acridine, 9-amino-3,6-dimethoxy-acridine, 9-acetamino-3,6-dimethoxy-acridine, 9-acetamino-3,6-dimethoxy-acridinium methyl iodide, 9-acetamino-3,6-dimethoxy-acridinium methyl *p*-toluenesulfonate and 9-amino-3,6-dimethoxy-acridinium methyl chloride.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN AROMATIC NITRO COMPOUNDS AND ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND ROY MCCRACKEN

RECEIVED JULY 19, 1928 PUBLISHED MARCH 6, 1929

Introduction

The reaction between aromatic nitro compounds and organomagnesium halides is complex and confusing. Earlier work by several others shows wide differences in the nature of the final products. The present results indicate that the course or courses of the reaction vary considerably with such conditions as temperature, relative quantities of reagents, type of Grignard reagent (alkyl or aryl MgX) and on whether the RMgX compound is prepared prior to or during the reaction with the nitro compound.

Historical Part

Yocich[1] obtained an unidentified hydrocarbon of the formula $C_{16}H_{10}$, melting at 87–88.5°, from the reaction between nitrobenzene and phenylacetenylmagnesium bromide, $C_6H_5C{\equiv}CMgBr$. We have repeated this work and have shown that his hydrocarbon was diphenyl-di-acetylene, $C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5$. Oddo[2] isolated a yellow compound from the reaction between nitrobenzene and ethylmagnesium iodide. This compound, to which he ascribed the formula $C_6H_5N({=}O)C_2H_5(OMgI)$, gave, on hydrolysis, ethylaniline and a red uncrystallizable oil that was not identified.

Pickard and Kenyon[3] in a short note containing the results of some preliminary experiments of the action of RMgX compounds on aromatic nitro compounds state that *p*-nitrotoluene reacts very vigorously with organomagnesium halides in ether solution, forming an amorphous yellow compound. This compound when hydrolyzed with acids yielded principally p-nitrosotoluene, p-tolylhydroxylamine, *p,p'*-azoxytoluene and *p*-toluidine. It is unfortunate that further details were not published because the products obtained by them have not been reported by others, unless we except the small quantity of the corresponding aniline obtained in some of our studies.

Schmidlin and Hodgson[4] obtained triphenylcarbinol from the reaction between *m*-nitrobenzaldehyde and triphenylmethylmagnesium chloride. They are inclined to attribute the formation of the carbinol to a splitting reaction of diethyl ether by the Grignard reagent. Straus[5] used *p*-nitro-

---

[1] **Yocich, J. Russ. Phys**-*Chem. Soc.*, **35,** 555 (1903).

[2] **Oddo,** *Atti. Accad. Lincei, (V)***13, ii,** 220 (1904); (**J.** *Chem. Soc., 1904,* 1,862).

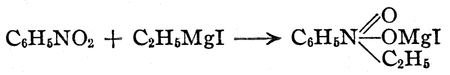
[3] **Pickard and** Kenyon, *Proc.* **Chem.** *Soc.*, **23,153** (1907).

[4] **Schmidlin and Hodgson,** *Ber.*, **41,430** (1908).

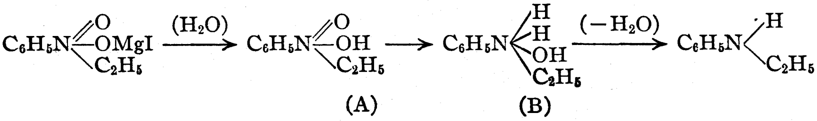
[5] Straus, *Ann.*, **393,235** (1912).

benzoyl chloride to characterize the -OMgX group in a substituted pentanol but instead of the expected *p*-nitrobenzoate he obtained a compound free of nitrogen and chlorine.

Hepworth[6] carried out a comprehensive investigation on the action of methylmagnesium iodide and ethylmagnesium bromide on nitrobenzene, *o*- and *p*-nitrotoluene and α-nitronaphthalene. In his experiments the Grignard reagent was prepared in the presence of the nitro compound by adding a mixture of the nitro compound and alkyl halide in ether to well-cooled ether containing powdered magnesium. By using about two moles of Grignard reagent per mole of nitro compound he obtained the respective alkylanilines and the azo compound corresponding with the nitro compound. Under the conditions of his experiments some unused nitro compound was generally recovered and he did not observe the formation of nitroso, hydroxylamine or azoxy compounds. He confirmed the formation of Oddo's[2] $C_6H_5N({=}O)C_2H_5(OMgI)$, but he disagrees with some of the following reactions proposed by Oddo.

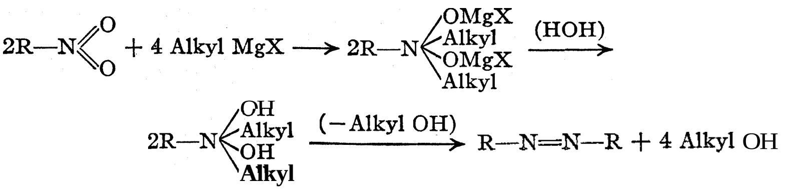


$$C_6H_5NO_2 + C_2H_5MgI \longrightarrow C_6H_5N\begin{cases}{=}O\\ -OMgI\\ -C_2H_5\end{cases} \qquad (I)$$



$$C_6H_5N\begin{cases}{=}O\\ -OMgI\\ -C_2H_5\end{cases} \xrightarrow{(H_2O)} \underset{(A)}{C_6H_5N\begin{cases}{=}O\\ -OH\\ -C_2H_5\end{cases}} \longrightarrow \underset{(B)}{C_6H_5N\begin{cases}-H\\ -H\\ -OH\\ -C_2H_5\end{cases}} \xrightarrow{(-H_2O)} C_6H_5N\begin{cases}-H\\ -C_2H_5\end{cases} \qquad (II)$$

Hepworth questions the intermediate formation of Compound (B), but sees no objection to postulating the direct loss of oxygen from Compound (A) to give ethylaniline. Admitting the difficulty of predicting the behavior of an unknown type like Compound (A), he suggests that "the loss of oxygen from such a compound is no more remarkable than the loss of carbon dioxide in the conversion of the simple monocarboxylic acid into the corresponding hydrocarbon, the more so if one accepts, what is probably the case, that Compound (A) is very unstable and just as likely to lose oxygen as Compound (B) is to lose water." He explains the formation of his azo compounds by the addition of two molecules of RMgX to his nitro compound to give an intermediate compound, two molecules of which, by the loss of four molecules of Alkyl OH compound, couple as follows



$$2R{-}N\begin{cases}{=}O\\ {=}O\end{cases} + 4\text{ Alkyl MgX} \longrightarrow 2R{-}N\begin{cases}-OMgX\\ -\text{Alkyl}\\ -OMgX\\ -\text{Alkyl}\end{cases} \xrightarrow{(HOH)}$$

$$2R{-}N\begin{cases}-OH\\ -\text{Alkyl}\\ -OH\\ -\text{Alkyl}\end{cases} \xrightarrow{(-\text{Alkyl OH})} R{-}N{=}N{-}R + 4\text{ Alkyl OH} \qquad (III)$$

---

[6] Hepworth, *J. Chem. Soc.*, 117,1004 (1920).

Tanasescu[7] measured the volume of gas evolved in the Zerewitinoff analysis of o-nitrobenzaldehyde with methylmagnesium iodide. Gilman and Fothergill[8] then showed that Tanasescu was incorrect in attributing to o-nitrobenzaldehyde a cyclic hydroxy formula on the basis of gas evolved with methylmagnesium iodide, inasmuch as such gas evolution is an inherent property of aryl nitro compounds. Later, Gilman and Fothergill[9] extended their studies on the interference of nitro groups on the Zerewitinoff method for the quantitative estimation of active hydrogen.

Recent work by Mingoia[10] reports the formation of di-indyl-*m*-nitrobenzylidene from *m*-nitrobenzaldehyde and indylmagnesium bromide, and of di-α-methylindyl-*m*-nitrobenzylidene from the same aldehyde and a-methyl-indylmagnesium bromide. These results are somewhat surprising, for in view of the high reactivity of the aryl nitro group it might have been predicted that the nitro group would have been attacked at least concurrently with the action of the -CMgX compound on the aldehyde group.

Nitrosyl chloride (NO_2Cl) and nitrosyl bromide gave no nitrobenzene with phenylmagnesium bromide.[11] The products isolated were diphenyl and chlorobenzene or bromobenzene. References to reactions between the Grignard reagent and nitroparaffins, several oxides of nitrogen and a wide variety of compounds containing the nitroso group are to be found in a recent paper by Gilman and McCracken[12] on the reaction between nitrosobenzene and phenylmagnesium bromide.

Discussion of Reactions

Under the conditions of our experiments we have found-that about four moles of Grignard reagent are necessary for each mole of nitro compound before obtaining the positive color test described by Gilman and Schulze[13] for reactive organometallic compounds. In addition to the secondary amine and ROH compounds, there also was obtained *a* very large quantity of R-R compound, essentially equivalent to the amount of ROH compound formed. Other compounds formed in very small quantities were *p*-phenyldiphenyl (when phenylmagnesium bromide was used), di-p-tolyl (when benzylmagnesium chloride was used) and aniline (when nitrobenzene was used). No azobenzene was obtained nor did we succeed (under our conditions) in isolating any nitroso, hydroxylamine or azoxy compounds. Special efforts were made in some experiments to isolate nitroso compounds that may have been formed at an intermediate stage.

---

[7] Tanasescu, Bull. *soc. chim.*, **39, 1443 (1926).**

[8] Gilman **and** Fothergill, THIS JOURNAL, **49,2815 (1627).**

[9] Gilman **and** Fothergill, *ibid.*, **50,867 (1928).**

[10] Mingoia, *Gazz. chim. ital.*, **56,772 (1926);** *C. A.*, **21, 1117 (1927).**

[11] Zuskine, Bull. *soc. chim.*, **37,187 (1925).**

[12] Gilman **and** McCracken, THIS JOURNAL, **49, 1052 (1927).**

[13] Gilman **and** Schulze, *ibid.*, **47,2002 (1925);** *Bull. soc. chim.*, **41, 1479 (1927).**

With alkylmagnesium halides the course of reaction appears to differ markedly from that when arylmagnesium halides were treated with the same nitro compound. For example, nitrobenzene with benzylmagnesium chloride gave 1,2-diphenyl-1,2-dibenzylhydrazine, $(C_6H_5)(C_6H_5CH_2)NN(CH_2C_6H_5)(C_6H_5)$. A special search for tetraphenylhydrazine that might have resulted from nitrobenzene and phenylmagnesium bromide failed to reveal any of this compound. Furthermore, it was shown that tetraphenylhydrazine underwent no noticeable reaction with phenylmagnesium bromide under conditions that simulated those used in the nitro reactions.

The equations proposed by Oddo[2] and by Hepworth[6] (see Reactions I, II and III) do not present a complete picture of the reaction. First, four and not one nor two moles of Grignard reagent are required for each mole of nitro compound; and, under the conditions of our experiments, when an insufficient quantity of Grignard reagent to complete the Reaction was added, small amounts of all of our end-products were isolated, together with unattacked nitro compound. In one of Hepworth's reactions between p-nitrotoluene and alkylmagnesium halides the use of four equivalents of Grignard reagent merely increased the quantities of alkyl-*p*-toluidine, and even with this ratio there was some unaltered nitro compound. This illustrates in a striking manner the different reactions that take place when the RMgX compound is formed in the presence of nitro compound. Second, neither of their explanations takes into consideration the formation of R-R compound by a coupling reaction of the organomagnesium halide. Third, Oddo's reaction scheme makes no provision for the formation of ROH compound, and Hepworth's interpretation correlates the formation of ROH compound (the isolation of which, by the way, was not described in his experiments) with azo compound, whereas in our studies large quantities of ROH compound were obtained when no azo compound was isolated.

Some support of the intermediate acidic compound (A in Reaction II) and its direct loss of oxygen to give the secondary amine may be found in related reactions. For example, it has long been known that oxygen and chloropicrin induce marked luminescence with Grignard reagents, particularly with p-chlorophenylmagnesium bromide. Unpublished studies show that such luminescence is an inherent property of nitro compounds. Quite likely the nitro compounds behave as oxidizing agents toward RMgX compounds and such oxidation in general is known to induce chemiluminescence.[14] Also, *p*-phenyldiphenyl has been obtained in small quantities by the oxidation of phenylmagnesium bromide.[15]

The formation of R-R compound may go hand in hand with the apparent absence of azo compound in our experiments, inasmuch as azo compounds

---

[14] Gilman and Adams, THIS JOURNAL, 47, 2816 (1925).

[15] Wuyts, *Compt. rend.*, 148, 930 (1909).

are known to react with Grignard reagents to give hydrazobenzene and R-groups which may couple to give R-R compounds or disproportionate to the corresponding olefinic and saturated hydrocarbons.[16] However, the R-R compound may also owe its formation to some other reaction or reactions, inasmuch as the reduction of azo compound should have yielded corresponding quantities of hydrazo compound. Hydrazo compounds have not as yet been identified and if such compounds were formed in appreciable quantities the method of working up the reaction products should have yielded large quantities of the corresponding azo compound as a consequence of the ready oxidation of hydrazo compounds.

For the present it may suffice to represent the reaction between nitrobenzene and phenylmagnesium hromide (a typical arylmagnesium halide) as follows

$$C_6H_5NO_2 + 4C_6H_5MgBr \xrightarrow{(H_2O)} (C_6H_5)_2NH + C_6H_5OH + C_6H_5C_6H_5 \qquad \textbf{(IV)}$$

At best such a representation is somewhat superficial and does not take into consideration the several concurrent and successive reactions that undoubtedly occur, the explanation of which must wait on an examination now in progress of the apparently intractable oils formed in these reactions. We have no experimental proof, at this time, for the mode of formation of the tetra-substituted hydrazines when alkylmagnesium halides are used. Alkylmagnesium halides are known to act in some cases as strong reducing agents, liberating olefinic hydrocarbons,[17] and we may be dealing here with addition of and reduction by the alkylmagnesium halide to give divalent nitrogen residues which then associate to tetra-substituted hydrazines.

Experimental Part

Details will be given here for a typical run between nitrobenzene and phenylmagnesium bromide. Table I contains an account of the several products obtained and their quantities. From the yields of phenol and diphenyl given in Table I there have already been deducted the quantities of these compounds present in the stock solution of phenylmagnesium bromide prior to reaction with nitro compound. In each 0.1 mole of this stock solution there were about 0.15 g. of phenol and 0.6 g. of diphenyl.

The nitrobenzene (24.6 g. or 0.2 mole) was dissolved in 200 ec. of dry ether in a one-liter three-necked flask provided with a mechanical stirrer, reflux condenser and a separatory funnel. Phenylmagnesium bromide was added dropwise with stirring and the reaction mixture was cooled with running water. After the addition of 0.4 mole of the Grignard reagent during one hour, a test[13] portion showed no RMgX compound; 0.2 mole more of phenylmagnesium bromide was added and the mixture gave no color

---

[16] Gilman and Pickens, THIS JOURNAL, 47, 2406 (1925); Gilman and Adams, ibid., 48,2004 (1926); Gilman and Fothergill, *ibid.*, 50,867 (1928) (see footnote 5 on p. 868); Rheinboldt and Kirberg, *J. prakt. Chem.*, 118, 1 (1928).

[17] See refs. 8 and 9 of this paper, in which attention is directed to the evolution of such unsaturated hydrocarbons when nitro compounds are treated with alkylmagnesium halides.

TABLE IA

REAGENTS

	Nitro compound	G.	Moles	RMgX	Moles
1	$C_6H_5NO_2$	23.6	0.2	C_6H_5MgBr	0.8
2	$C_6H_5NO_2$	24.6	.2	C_6H_5MgBr[a]	.8
3	α-$C_{10}H_7NO_2$	17.3	.1	C_6H_5MgBr	.7
4	$C_6H_5NO_2$	12.3	.1	$C_6H_5C{\equiv}CMgI$[b]	.1
5	o-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.6
6	o-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.3
7	o-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.2
8	o-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.1
9	p-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.6

[a] In this experiment the phenylmagnesium bromide was prepared in the presence of nitrobenzene to simulate the conditions of Hepworth[a] in order to obtain, if possible, something like the relatively large amounts of azobenzene he secured. However, because it was impossible to make bromobenzene react with magnesium in the presence of nitrobenzene at low temperatures (−15°), the reaction was carried out without cooling, under which condition it proceeded smoothly. The mixture of bromobenzene and nitrobenzene in ether was added during three hours and after refluxing for two hours the mixture was hydrolyzed with 400 cc. of a saturated ammonium chloride solution. About 0.5 g. of aniline was obtained in this experiment but no azobenzene nor unaltered nitrobenzene. There was a large quantity of unidentified tarry product in this experiment.

[b] This experiment was carried out with the sole purpose of identifying Yocich's[1] hydrocarbon ($C_{16}H_{10}$) melting at 87–88.5°. Among the reaction products was 2 g. of diphenyl-di-acetylene melting at 88°. Its identity was confirmed by a mixed melting point determination and by the preparation of the picrate, which melted at 108°. In addition to 8.8 g. of recovered nitrobenzene, there was obtained one g. of phenylacetylene iodide ($C_6H_5CI{=}CHI$) melting at 76° and showing no depression in a mixed melting point determination with an authentic specimen. This di-iodo compound may owe its formation to a reaction between the small excess of phenylacetylene and some iodine resulting from the ethylmagnesium iodide used in the preparation of the phenylacetenylmagnesium iodide.

TABLE IB

PRODUCTS

	Amine	G.	Phenol, g.	Diphenyl, g.	p-$C_6H_5C_6H_4C_6H_5$, g.
1	$(C_6H_5)_2NH$	19.5	15.5	24.5	1.0
2	$(C_6H_5)_2NH$	9.5	8.8	19.7	0.5
3	$(\alpha$-$C_{10}H_7)(C_6H_5)NH$[a]	7.8	...	..	...
4	....	..	..	..	...
5	$(o$-$C_7H_8)(C_6H_5)NH$	10.8[b]	7.9	14.8	0.5
6	$(o$-$C_7H_8)(C_6H_5)NH$	9.7[b]	7.8	4.7	0.1
7	$(o$-$C_7H_8)(C_6H_5)NH$	4.4[b]	4.97	3.7	...
8	$(o$-$C_7H_8)(C_6H_5)NH$	2.2[b]	3.52	..	...
9	$(p$-$C_7H_8)(C_6H_5)NH$	8.7	7.9	14.0	1.0

[a] The only product looked for here was the phenyl-α-naphthylamine in order to ascertain the value of this reaction for the preparation of some secondary aromatic amines.

[b] Expts. 5, 6, 7 and 8 are illustrative of the effects of varying quantities of Grignard reagent with a given quantity of nitro compound. No o-nitrotoluene was recovered in Expts. 5 and 6 but the quantities recovered in Expts. 7 and 8 were 2.7 g. (19.7%) and 7.6 g. (54.7%), respectively.

test[13] at the end of five hours; 0.1 mole more gave no test after twelve hours, and an additional 0.1 mole reacted within twenty-four hours. The total quantity of phenylmagnesium bromide added was about 0.8 mole or four equivalents per equivalent of nitrobenzene; the total time of reaction was forty-two hours. Several experiments showed that the addition of phenylmagnesium bromide in excess of four equivalents gave a color test that persisted, In some other studies on the rates of reaction of various compounds with the Grignard reagent, it has been shown that two equivalents of n-butyl- and of phenylmagnesiumbromide are used up almost at once (within five minutes) when added to 0.1 mole of nitrobenzene in an ether solution that is refluxed.

The reaction mixture was then decomposed in a few cases with cold, dilute hydrochloric acid or more generally by a saturated ammonium chloride solution. The ether layer was separated and extracted with two 100-cc. portions of 10% sodium hydroxide. The phenol obtained by acidification of this extract followed by ether extraction and distillation weighed 15.5 g. and boiled at 180–182°. In many experiments the phenol was recovered and weighed as tribromophenol. The reaction was carried out in an atmosphere of hydrogen because the extended time of reaction would have resulted in most of the Grignard reagent being oxidized to phenol by atmospheric oxygen.

The ether layer was dried with sodium sulfate, filtered and treated with hydrogen chloride to precipitate the hydrochlorides of the amines. The crude hydrochloride was filtered and treated with sodium hydroxide to liberate the amine, which was extracted with ether and purified by vacuum distillation. In this manner 19.5 g. of diphenylamine was obtained boiling at 176–178° (20 mm.) and melting at 50°. A mixed melting point determination with an authentic specimen of diphenylamine melted at 52°.

The ether filtrate from the hydrochloride precipitate was fractionally distilled. Redistillation of a first fraction (25.5 g. distilling between 240–275° and melting at 63–67°) gave 21 g. of diphenyl that distilled at 252–256° and melted at 69–70°. The residue of this first fraction was added to a second fraction (boiling between 275° (740 mm.) and 250° (30 mm.) and weighing 9.2 g.) and the combined portions were dissolved in benzene and treated with hydrogen chloride to assure complete removal of the amine. No amine hydrochloride precipitated on this treatment. This benzene solution, when distilled in a vacuum, gave an additional 3.5 g. of diphenyl (making a total of 24.5 g. of diphenyl), and one g. of *p*-phenyldiphenyl that melted at 203° after crystallization from alcohol. In every case, where possible, the identity of solids was confirmed by mixed melting point determinations made with authentic specimens.

Reaction between Nitrobenzene and Benzylmagnesium Chloride.—In view of the products obtained from the reaction between nitrobenzene and phenylmagnesium bromide, we expected the reaction between nitrobenzene and benzylmagnesium chloride to proceed after the general scheme represented in Reaction IV and to give, accordingly, benzylaniline, benzyl alcohol and dibenzyl. However, unusual difficulty was experienced in working up the basic fractions and the isolation of benzaldehyde prompted a number of experiments the object of which was to throw some light on the formation of the aldehyde and the difficulty of obtaining the expected benzylaniline. In view of the final identification of the 1,2-diphenyl-1,2-dibenzylhydrazine, it is unnecessary at this time to give an account of these several orienting experiments.

Thirty and eight-tenths g. (0.25 mole) of nitrobenzene was added slowly with stirring to one mole of benzylmagnesium chloride kept cool by running water. After allowing the reaction mixture to stand overnight, it was hydrolyzed by 100 cc. of water. The dark-colored oil obtained from the ether layer when fractionally distilled in a vacuum yielded 2.5 g. of aniline (identified,by the formation of benzanilide and *p*-nitrobenzanilide), 22.6 g. of dibenzyl (after deducting the quantity of dibenzyl formed in the preparation of benzylmagnesium chloride), 3 g. of *p*-ditolyl and a basic fraction which when treated in ether solution with hydrogen chloride gave 4.5 g. of a hydrochloride.

This hydrochloride was formed from 12.2 g. of a basic fraction that distilled over a wide temperature range, 150° (10 mm.) to 200° (5 mm.). After crystallization from an alcoholic hydrogen chloride solution, the salt melted at 213°. When refluxed with dilute hydrochloric acid it yielded benzaldehyde (identified by the phenylhydrazone), aniline (identified as tribromoaniline) and benzylaniline (identified as the hydrochloride). The derivatives of all three products of hydrolysis were identified in turn by mixed melting point determinations made with authentic specimens of the corresponding compounds.

Franzen and Zimmermann[18] first prepared 1,2-diphenyl-1,2-dibenzylhydrazine hydrochloride and found it to melt at 215.5°. On acid hydrolysis they obtained from it benzaldehyde, aniline and benzylaniline. Later, Wieland and Fressel[19] attempted to prepare the tetra-substituted hydrazine by the method used by Franzen and Zimmermann, by heating the corresponding tetrazene. However, they observed that the high temperature necessary to distil the hydrazine is sufficient to decompose this compound; and the distillation of the tetrazene yielded benzylaniline and benzalaniline. Acid hydrolysis would accordingly break down the benzalaniline to give benzaldehyde and aniline, so that the three products obtained by Franzen and Zimmermann from the hydrolysis of their supposed 1,2-diphenyl-1,2-dibenzylhydrazine would come, in reality, from the two decomposition products of their hydrazine, benzylaniline and benzalaniline. The high melting point (215.5') observed by Franzen and Zimmermann is explained by Wieland and Fressel as being due to rapid heating. However. it should be recalled that we identified our benzylaniline by the melting point of the corresponding hydrochloride and under our conditions of determining melting points it agreed with the correct point as given in the literature.

For our present purposes it does not make any difference whether we had in hand the hydrazine or its decomposition products (benzylaniline and benzalaniline), inasmuch as the compounds obtained by Franzen and Zimmermann and by Wieland and Fressel were prepared by a standard procedure for the preparation of such hydrazines and because Wieland and Fressel admit that their decomposition products (benzylaniline and benzalaniline) came from the tetra-substituted hydrazine.

Reaction between Nitrobenzene and Ethylmagnesium Bromide.—By analogy with the benzylmagnesium chloride reaction, one would expect to get 1,2-diphenyl-1,2-diethylhydrazine from the reaction between nitrobenzene and ethylmagnesium bromide. Experiment verified this. Wieland and Fressel[19] found this hydrazine to be unstable and to undergo considerable decomposition even when distilled in a high vacuum. The boiling point of their compound was 141° (1 rnm.). Our hydrazine boiled at 118–123° (0.5 mm. (or less)). Hydrolysis by heating with dilute hydrochloric acid gave the products described by Wieland and Fressel,[19] namely acetaldehyde, aniline and ethylaniline. However, our compound did not give the characteristic color reaction with acetic acid that they described. This was not wholly unexpected, inasmuch as Gilman and Pickens[20] prepared this hydrazine from azobenzene, phenylmagnesium bromide and diethyl sulfate, and found it to distil at 140–145° (1.5 mrn.), but not to give the color test. The reason for this discrepancy is to be found in the observation of Wieland and Fressel[19] that the tetrazene from which their hydrazine was prepared also gives the color test. Very probably their hydrazine was contaminated with some tetrazene.

---

[18] Franzen and Zimmermann, *Ber.*, 39,2566 (1906).

[19] Wieland and Fressel, *Ann.*, 392, 150 (1912).

[20] Gilman and Pickens, THIS JOURNAL, 47,2406,2412 (1925)

The formation of the hydrazine prompted a repetition of Hepworth's[6] experiment in which nitrobenzene and ethyl bromide were added to magnesium in ether to give ethylaniline and azobenzene. We found that the ethylaniline fraction boiled over a wide range (200–270°) when first distilled at atmospheric pressure. The fraction containing ethylaniline also gave qualitative tests for the hydrazine (acetaldehyde on acid hydrolysis) and for aniline. From this one may conclude that the hydrazine is one of the products of reaction and that a part, at least, of their and our ethylaniline may have resulted from the known course of thermal decomposition of the hydrazine to give ethylaniline.

Attempted Isolation of **Tetraphenylhydrazine** and its Treatment with **Phenyl-** and ***n*-Butylmagnesium** Bromides.—Several reactions were carried out between nitrobenzene and phenylmagnesium bromide with the express purpose of either identifying or isolating tetraphenylhydrazine or its rearrangement products. All of these unsuccessful experiments were made after it was shown that alkylmagnesium halides with nitrobenzene gave tetra-substituted hydrazines. The respective fractions that might have contained the tetraphenylhydrazine neither gave the characteristic color test[21] for the hydrazine nor did they yield the sparingly soluble diphenylbenzidine[21] that results from the rearrangement of tetraphenylhydrazine by concd. sulfuric acid.

Also, no reaction appeared to take place when 25.4 g. (0.08 mole) of tetraphenylhydrazine in 500 cc. of ether and 200 cc. of benzene was treated with 0.1 mole of phenylmagnesium bromide for fifteen hours at room temperature. On working up the reaction product in the customary manner, there was recovered 22.5 g. (85.2%) of the tetraphenylhydrazine. A less exact experiment with tetraphenylhydrazine (5 g.) and n-butylmagnesium bromide (0.05 mole) showed no evidence of reaction and most of the hydrazine was recovered.

Attempts to Isolate an Intermediate **Nitroso** Compound.—From 61.5 g. (0.5 mole) of nitrobenzene and 1.0 mole of phenylmagnesium bromide there was obtained 17.7 *g.* of phenol and 18 g. of unaltered nitrobenzene, but no nitrosobenzene. The high yield of phenol obtained here and the yields of phenol described in Expts. 6, 7 and 8 (Table I) indicate that the successive reactions leading to the formation of phenol proceed more rapidly than the initial reaction with nitro compound.

Equally unsuccessful attempts were made to isolate nitrosobenzene in several experiments in which the temperature and the ratio of nitrobenzene to RMgX were varied. In only one experiment was there a faint green color during the steam distillation procedure employed to remove any nitrosobenzene.

Attention was then directed to the possibility of isolating a more stable nitroso compound, p-nitrosodimethylaniline, when p-nitrodimethylaniline was used as the initial compound. However from 16.6 *g.* (0.1 mole) of *p*-nitrodimethylaniline and 0.1 mole of phenylmagnesium bromide there was recovered 7.8 g. (47%) of the nitro compound, but no p-nitrosodimethylaniline. From another experiment starting with 0.1 mole of p-nitrodimethylaniline and 0.4 mole of phenylmagnesium bromide there were isolated 4.4 g. of phenol, 5 *g.* of diphenyl and 5 6 g. of an intractable amino compound that may have been *p*-dimethylaminodiphenylamine.[22]

Reaction between Dimethylaniline Oxide and Phenylmagnesium Bromide.-—The $R(Alkyl)_2N(OH)_2$ intermediate postulated by Hepworth[6] (see Reaction III) might be expected to lose water and form a dialkylaniline oxide. For this reason, 27.4 g. (0.2 mole) of dimethylaniline oxide partially dissolved in 600 cc. of warm (40") benzene was treated with 0.4 mole of phenylmagnesium bromide. The following products were isolated: phenol (3.56 *g.*), diphenyl (8.6 g) and dimethylaniline (2 5 g). The am-

---

[21] Wieland and Gambarjan, Ber., **39,** 1499 (1906).

[22] Ref. 12, pp. 1060–1061.

moniacal solution obtained on hydrolysis yielded a very small quantity of a solid that dissolved readily in hydrochloric acid giving a purple color.

Reaction between Ethyl Nitrate and Phenylmagnesium Bromide.—This reaction was carried out at a very low temperature (about −80°) to determine whether nitrobenzene might be formed in accordance with the following reaction

$$C_6H_5MgBr + C_2H_5ONO_2 \longrightarrow C_6H_5NO_2 + C_2H_5O(MgBr) \qquad (V)$$

Kinkead[23] previously studied this reaction at about 0° and reported the production of a blue solution on extraction with chloroform, which had the properties of an indicator. **Hepworth**,[24] at −15°, obtained dimethylhydroxylamine, $(CH_3)_2NOH$, and diethylhydroxylamine from methyl- and ethylmagnesium halides, respectively.

When 0.2 mole of phenylmagnesium bromide was added dropwise and with stirring to 0.3 mole of ethyl nitrate cooled by a slush of carbon dioxide and acetone, diphenyl and phenol were obtained but no nitrobenzene.

Summary

The products obtained in the reaction between aryl nitro compounds and organomagnesium halides vary markedly with experimental conditions. Under the conditions of the experiments described here, the following general reaction takes place

$$C_6H_5NO_2 + 4C_6H_5MgBr \longrightarrow (C_6H_5)_2NH + C_6H_5OH + C_6H_5{\cdot}C_6H_5$$

With alkylmagnesium halides, tetra-substituted hydrazines are among the reaction products. Ethylmagnesium bromide and nitrobenzene, for example, give 1,2-diphenyl-1,2-diethylhydrazine, $(C_6H_5)(C_2H_5)NN(C_2H_5)(C_6H_5)$. The formation of alkylanilines in this reaction is due in part to the decomposition of such hydrazines.

AMES, IOWA

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OR AGRICULTURE]

THE PROPERTIES AND CHEMICAL CONSTITUTION OF GLUCIC ACID

BY E. K. NELSON AND C. A. BROWNE

RECEIVED SEPTEMBER 21, 1928 PUBLISHED MARCH 6, 1929

H. Winter,[1] while working in the laboratory of Fraser Eaton and Company, Soerabaya, Java, announced in 1894 that upon warming an aqueous solution of 1% invert sugar with 0.5% of calcium oxide in the form of calcium hydroxide at 66.5°, he obtained a voluminous, white flocky precipitate which redissolved on further heating. This precipitate turned brown on exposure to the air and because of its slimy character could not be filtered readily. Winter purified the precipitate, which he supposed to be a basic calcium salt, by decanting and washing five times with lime water, the settling of the precipitate being performed in a well-closed flask, filled

---

[23] Kinkead, *Chem. News*, **122**, 4 (1921).

[24] Hepworth, *J. Chem. Soc.*, **119**, 251 (1921).

[1] Winter, *Z. Ver. Rübenzucker Ind.*, 44 (old series), 1049 (1894).

completely full in order to exclude the air. The unchanged white precipitate was then decomposed with dilute sulfuric acid and extracted with ether. Evaporation of the ether upon a watch glass left behind colorless, needle-like crystals of an organic acid in a yellow, sirupy mother liquor.

On repeating the experiment with 24 liters of invert sugar solution, Winter obtained a small amount of a yellow sirup filled with beautiful crystals 3–4 mm. long. After being placed in a desiccator over sulfuric acid the crystalline needles appeared in a few days to melt away and nothing was left in the sirup but some undeveloped crystals resembling cane sugar in appearance. After some time the sugar-like crystals also began to disappear with a darkening of color and a slight evolution of gas which ceased only after the residue had solidified to a dark resinous mass. The latter, upon distillation with water, yielded carbon dioxide and formic acid, leaving behind a residue of brown-colored flocks.

Winter's efforts to purify the substance by recrystallization from water, alcohol, ether or chloroform were unsuccessful. An aqueous solution of the crystals reduced Fehling's solution in the cold and precipitated black silver immediately from silver nitrate. From these results Winter supposed that the impure crystals of his experiment might be the so-called glucic acid, which Peligot,[2] Mulder,[3] Reichardt[4] and other investigators had never succeeded in isolating in the crystalline form, and which Winter further supposed to undergo on standing a slow transition into apoglucic acid with final decomposition into carbon dioxide, formic acid and other products. As much confusion prevails in the literature concerning the substance to which Dumas first gave the name of "glucic acid," the present study was initiated in the hope of determining more exactly the nature of the unstable acid compound that was obtained by Winter as a result of the action of calcium hydroxide upon invert sugar.

Experimental

The experiment of Winter was repeated except that dextrose (commercial "Cerelose") was used in place of invert sugar. In the preliminary test fifty grams of dextrose dissolved in five liters of water was heated at 67° with 25 g. of calcium oxide which had previously been well slaked in water. The precipitate which settled out on cooling was filtered, washed with lime water, decomposed with sulfuric acid and the calcium sulfate removed by filtration. The filtrate was thoroughly extracted with ether; on evaporation of the ether a small amount of crystalline material associated with a sharp-smelling liquid remained. The crystals were separated from the liquid on a porous plate.

---

[2] Peligot, *Ann.*, 30, 76 (1839).

[3] Mulder, *Bulletin des sciences physiques et naturelles en Neerlande,* 1–102 (1840), abstracted in *Ann.,* 36,243–295 (1840).

[4] Reichardt, *Z. Ver. Rübenzucker Ind.*, 20 (old series), 529 (1870).

As Winter states that the precipitated calcium compound is somewhat soluble in water, it was thought that increasing the concentration might improve the yield. This proved to be the case and the following procedure was adopted. With further improvement in technique it is possible that the yield may be still further increased.

Four hundred grams of dextrose, 5 liters of water and **100** g. of calcium oxide (slaked) mere thoroughly mixed with a stream of illuminating gas in order to avoid oxidation by air and heated to 67°.

On cooling a voluminous precipitate (A) separated. This was filtered, washed with lime water and finally with alcohol and ether, care being taken to avoid the passage of air through the filter by keeping the precipitate covered with a layer of liquid.

The precipitate was dried in a vacuum desiccator, contact with air being avoided, and when dry it was kept in an atmosphere of illuminating gas.

A preparation of the calcium compound, dried in illuminating gas, rapidly rose in temperature from 20° to 48° when exposed to the air. After exposure to air overnight it yielded only a trace of crystalline substance, the resulting product appearing to be a mixture of formic acid and a liquid, oily acid. That the heating of the substance is due to absorption of oxygen was proved by the following experiment.

A quantity of the precipitate was placed in a flask attached to a train consisting of a U-tube containing liquid paraffin and a drying tube containing calcium chloride, the latter tube being connected with a supply of oxygen. The steady absorption of oxygen for many hours was noted by the bubbling through the U-tube.

The dried precipitate (A) weighed **118.6** g. and contained **30.3** g. of calcium oxide.

The calculated amount of sulfuric acid necessary to combine with the **30.3** g. of calcium oxide was diluted, cooled with ice and added to the ice-cooled suspension of the precipitate. The mixture was thoroughly agitated until the reaction was complete, when the calcium sulfate was removed by filtration and washed. The filtrate (B) was concentrated in a vacuum distillation outfit connected with a receiver cooled by ice and salt (in order to lower the temperature of distillation) and with a stream of carbon dioxide passing through a capillary tube into the distilling flask to prevent bumping and to exclude air. The distillation was conducted in a vacuum of **20–30** millimeters.

The concentrated solution was extracted with ether in an extractor designed for extracting liquids with ether, so long as crystals were obtained on evaporation of the solvent. The total yield of crystalline material (C) was **1.34** g. in this experiment. The oily product absorbed by the porous plates was recovered by extraction with ether and reserved for future investigation.

The distillate obtained in concentrating the acids in the filtrate (B) required 189.5 cc. of $N/10$ barium hydroxide for its neutralization, which yielded upon evaporation **2.1802** g. of barium salt. Since 189.5 cc. of $N/10$ barium hydroxide is equivalent to **2.1542** g. of barium formate, the volatile acid obtained by decomposition of the calcium precipitate (A) with sulfuric acid is almost entirely formic acid. The fact that no alcohol-soluble lead salt was found after conversion of the barium compound into the lead derivative indicated the absence of acetic acid.

The crystalline acid (C), Winter's "glucic" acid, is easily soluble in water and alcohol, but only moderately soluble in ether, chloroform or ethyl acetate.

The substance was freed from liquid impurities by wetting with a little ethyl acetate and spreading on a porous plate. If left in contact with the liquid acid which accompanies it, the substance is very unstable. When the crystals wet with the liquid acid were left overnight in a desiccator, the solid substance almost disappeared and a brown, pasty mass was left. This confirms Winter's observations. **An** optical examination[5] gave the following results.

In ordinary light: The material consisted of plates. Its indices of refraction were $N\alpha = 1.475$, $N\gamma = 1.734$, both ±0.002. Birefringence was extremely strong. Between crossed Nicols it showed anomalous blue and purple polarization colors due to peculiar dispersion This may be of use in recognizing the substance. An aqueous solution of the compound does not rotate the plane of polarized light.

The substance partially sublimes in beautiful crystals at the temperature of the water-bath. The unsublimed portion appears to have polymerized, as it no longer crystallizes from water.

The compound has no definite melting point. It turns brown and polymerizes at temperatures over 110°. Heated to 170° there was no evidence of melting in the dark colored transformation product.

An aqueous solution of the compound reduces silver nitrate, Fehling's solution and mercuric chloride at room temperature, the reductions taking place suddenly after an instant of time. The solution does not give a normal aldehyde reaction with Schiff's reagent. After treatment with this reagent, a solution of the substance gradually develops a violet-blue color. When a solution of ferric chloride is added to a solution of the compound, the ferric chloride is reduced and a faint blue color is developed which instantly disappears. The evanescent blue color is more marked if a solution of the substance is carefully added to a solution of ferric chloride. A very delicate and beautiful reaction is given by treating the substance in aqueous solution with a few drops of a solution of sodium nitroprusside, a drop of 10% solution of sodium hydroxide and finally a drop or two of acetic acid. An intense greenish-blue to blue color results and, on standing, a blue lake is deposited, leaving a nearly colorless supernatant liquid.

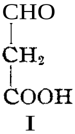
The substance is an acid and gives a sharp end-point on titration: 0.7333 g. = 16.27 cc. of $N/2$ NaOH. The neutralizing equivalent is therefore 90.

An analysis was made for carbon and hydrogen and the molecular weight was determined by the freezing-point method, using water as the solvent. The results obtained are as follows.

Anal. Calcd. for $C_3H_4O_3$: C, 40.89; H, 4.58; mol. wt., 88. Found: C, 40.53, 40.50, 40.66; H, 4.93, 4.73, 4.58; mol. wt., 88.4, 91.5, 94.9. The molecular weight appears to increase with the concentration, suggesting molecular aggregation.

A solution of the substance bleaches bromine water instantly; iodine absorption, calculated for one double bond, 288.3; found, 289, 285.

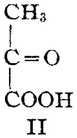
There are five possible constitutional formulas for an acid of the formula $C_3H_4O_3$.



$CHO-CH_2-COOH$

I

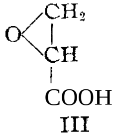
Semi malonic aldehyde



$CH_3-C{=}O-COOH$

II

Pyruvic acid



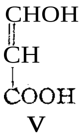
III

Glycidic acid

$CH_2{=}COH-COOH$

IV

α-Hydroxyacrylic acid



$CHOH{=}CH-COOH$

V

β-Hydroxyacrylic acid

The semialdehyde of malonic acid (I) should give an aldehyde reaction with Schiff's reagent, and should be oxidized easily into malonic acid, Pyruvic acid (11),a liquid, has properties altogether different from those of

---

[5] Made by G. L. Keenan, Food. Drug and Insecticide Administration, U. S. Department of Agriculture.

the acid under discussion. Moreover, when pyruvic acid is treated with sodium nitroprusside and alkali, a wine-red color is developed which is *discharged* on the addition of acetic acid. Glycidic acid (III) is a liquid, miscible with water, alcohol and ether. Its calcium salt readily takes up water, forming calcium glycerate, so that it could not be formed under the conditions of our experiments.

The ready absorption of bromine suggests the presence of a double bond as in IV and V, while the remarkable reducing properties indicate an aldehyde or an enolic form readily convertible into an aldehyde. These conditions seem to be best met by Formula V (β-hydroxy-acrylic acid), which is the enolic form of the semialdehyde of malonic acid.

Such a compound has been described by Pinner[6] under the name of "Acrolactic Acid," which was prepared by the action of barium hydroxide on monochloro-ethyl acrylate. The free acid was obtained as a sirup which showed a tendency to crystallize. On account of scarcity of material Pinner was unable to make an analysis. However, he states that acrolactic acid is extremely unstable, and, though not mentioning any direct experiments on its reducing properties, observes that its silver salt darkened at once.

The acid which we obtained appears to be fairly stable, if well separated from the liquid acid extracted with it and kept in a closed container in a cool place.

If the substance is acrolactic acid, it should yield formic and oxalic acids on gentle oxidation.

An excess of sodium hydroxide was added to an aqueous solution of 1 g. of the crystalline compound and the solution boiled for a short time. Sulfuric acid was added in slight excess and the solution was distilled. The distillate was neutralized with barium hydroxide and evaporated to dryness.

The barium salts weighed 0.6862 g., corresponding to 0.2781 g. of formic acid or 27.8% of the substance.

No acetic acid was found and optical examination showed the salt to consist entirely of barium formate.

One-half gram of the substance was oxidized with hydrogen peroxide in excess. After the addition of ammonia, ammonium chloride and calcium chloride, the solution was boiled. A copious precipitate resulted which weighed 0.3309 g., equivalent to 0.204 g. of oxalic acid, or 40.8% of the sample.

The precipitate was shown by optical methods to be calcium oxalate.

A preparation of Winter's glucic acid was hydrogenated, platinum dioxide and 0.0001 mole of ferric chloride being used. The absorption of hydrogen ceased after less than one-fifth of the calculated amount of gas necessary for completely hydrogenating a compound of the type of Formula

---

[6] Pinner, *Ber.*, 7,250 (1874); *Ann.*, **179**, 91 (1875).

V had been taken up. The substance recovered after hydrogenation was no longer crystalline and had the appearance of the polymerized product. It was thought that the ferric chloride might have caused polymerization and thus interfered with a normal hydrogen absorption.

The experiment was repeated, colloidal palladium being used as a catalyst: 0.3764 g. of substance absorbed 166 cc. of hydrogen at 25° arid 764.7 mm.; reduced to 0° and 760 mm. = 148.3 cc. or 0.01328 g. Calculated for two atoms of hydrogen absorbed by 0.3764 g. of mol. wt. 88, 0.00855 g.; and for three atoms, 0.01283 g. The product recovered after the reaction did not have an acid taste. It was highly soluble in water, very hygroscopic and scarcely soluble in ether. When dissolved in alcohol and precipitated with ether, an amorphous, very hygroscopic solid was obtained. It is evident again that a normal hydrogenation has not taken place, the product having probably suffered molecular change and polymerization.

It may be stated, finally, that the present investigation has not altogether confirmed the conclusion of Winter that his crystalline glucic acid undergoes first a transformation into apoglucic acid and then a further decomposition into carbon dioxide, formic acid and other products. No evidence was obtained in these experiments of the spontaneous decomposition of Winter's glucic acid into any such product as the apoglucic acid described by Mulder or into carbon dioxide, although abundant quantities of formic acid and of unidentified polymerization products were obtained.

The readiness with which glucic acid decomposes into formic acid leads to the conclusion that it may be a parent substance of the formic acid which occurs in the sirups and molasses of cane sugar factories, where the calcium hydroxide employed in clarification reacts with the reducing sugars of the juice. The instability of this compound in the presence of atmospheric oxygen and in contact with accompanying organic substances is no doubt the reason of its having escaped the attention of so many investigators.

The problem of the formation and decomposition of glucic acid under varying conditions is being subjected in this Laboratory to a further study in the hope that additional information may be secured upon some of the theoretical and practical questions involved.

Summary

1. The unstable calcium salt of an acid, originally described by Winter under the name of glucic acid, was prepared by the action of calcium hydroxide upon dextrose in aqueous solution at 67° in the absence of air. The precipitated calcium compound absorbed oxygen rapidly from the air with decomposition and evolution of heat.

2. The unstable calcium salt, after decomposing with sulfuric acid and extracting with ether, yielded a small amount of crystallizable unsaturated acid, corresponding to the formula $C_3H_4O_3$, which from its strong reducing

power, iodine absorption and other properties is in all probability the enolic form of the semialdehyde of malonic acid. The crystalline acid can be partially sublimed without decomposition but undergoes upon heating a considerable degree of polymerization. It yields formic and oxalic acids upon oxidation and is exceedingly unstable in the presence of organic impurities.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY, MEDICAL SCHOOL, UNIVERSITY OF CALIFORNIA]

THE RATE OF HYDROLYSIS OF CASEIN IN ACID SOLUTIONS AS MEASURED BY THE FORMATION OF AMINO NITROGEN

BY E. S. NASSET AND DAVID M. GREENBERG

RECEIVED OCTOBER 3, 1928 PUBLISHED MARCH 6, 1929

Introduction

Greenberg and Burk[1] from their own measurements and such data as were available, calculated the order of the reaction of the hydrolysis of the proteins in solutions of acids. The hydrolysis for gelatin, silk fibroin and gliadin was found to conform to the equation of a second order reaction. A single series of measurements on casein by Dunn[2] apparently fitted a first order reaction best. This was in agreement with the findings of Carpenter,[3] who worked, however, under radically different conditions. It seemed worth while to check the order of the reaction of the hydrolysis of casein, since if a universal structural basis is common to all proteins, individual proteins would not be expected to show different orders of hydrolysis under the same fixed conditions. From the results given in the following, it is to be seen that casein conforms to the proteins already measured and that the hydrolysis reaction is of the second order under the conditions employed. Also, as was found for the other proteins, the effect of acids in accelerating the rate of hydrolysis is shown to be proportional to the hydrogen-ion activity of the acid solutions.

Experimental

The measurements were carried out at the temperatures of 127.5, 117.5 and 105.5°, employing the acids, hydrochloric, sulfuric and phosphoric. The hydrolyses were carried out in an autoclave with a steam line the pressure of which could be regulated by a reducing valve. The casein used was prepared according to the method, somewhat modified, of Van Slyke and Baker.[4] One-gram samples of thoroughly dried casein were placed in 50-cc. pyrex Erlenmeyer flasks, 40 cc. of the desired acid was added and

---

[1] D. M. Greenberg and N. F. Burk, THIS JOURNAL, 49, 275 (1927).

[2] M. S. Dunn, *ibid*, 47, 2564 (1925).

[3] D. C. Carpenter, J. *Biol. Chem.*, 67, 647 (1926).

[4] L. L. Van Slyke and J. C. Baker, *ibid.*. 35, 128 (1918); D. M. Greenberg and C. L. A. Schmidt, J. Gen. *Physiol.*, 7, 287 (1924).

then the flasks were sealed with a blast lamp. This made the casein concentration in the acids 2.5%. In a few instances large pyrex test-tubes were employed, using half the above amounts of casein and acid. A series of such sealed flasks or tubes was placed in the autoclave and the steam turned on. At appropriate intervals duplicate flasks were removed from the autoclave and immediately immersed in ice water. The removal of these flasks was accomplished in about eighty seconds, so that the temperature of the remaining flasks did not fall appreciably before the temperature was restored to the working level. As soon as the flasks were cool, the seal was broken and the contents neutralized to prevent further hydrolysis. With the gram samples the final volume was made up to 100 cc., with the half-gram samples up to 50 cc. One-cc. amounts of these solutions were used for analysis of amino nitrogen by the Van Slyke method.[5] Duplicate analyses were made on each sample. As in the previous work, the increase in amino nitrogen was taken as measuring the amount of hydrolysis. In calculating the percentage of hydrolysis, the figure taken for total amino nitrogen was that given by Dunn, namely, 70% of the total nitrogen of casein.

The experimental results are given in Tables I to V. The column headings in the tables require no further explanation.

TABLE I

THE HYDROLYSIS OF CASEIN BY HYDROGEN CHLORIDE AT 127.5°

1.0 *N* Hydrochloric Acid

Time, hours	0.5	0.75	1.0	1.25	1.5	1.75	2.0
Amino N per g. of casein, mg.	43.3	51.2	56.3	61.4	65.2	68.2	68.9
Hydrolysis, %	45.7	54.3	59.5	64.8	68.9	72.2	72.8
K, vel. const., 1st order	0.53	0.46	0.39	0.36	0.34	0.32	0.28
K, vel. const., 2d order × 10^3	17	16	15	15	15	15	13
K, rel. const., 3d order × 10^4	2.4	2.5	2.6	2.8	3.1	3.4	3.2

$k/a_{\pm} = 0.019$. Average of second order constants $= 15 \times 10^{-3}$.

0.5 *N* Hydrochloric Acid

Time, hours	0.5	0.75	1.0	1.25	1.3
Amino N per g. of casein, mg.	31.3	37.5	44.4	46.9	50.1
Hydrolysis, %	33.1	39.6	46.9	49.6	52.8
K, 2d order const. × 10^3	9.9[a]	8.7	8.8	7.9	7.5

[a] Value not used in obtaining average.

$k/a_{\pm} = 0.021$. Average of constants, 8.2×10^{-3}.

TABLE II

THE HYDROLYSIS OF CASEIN BY HYDROGEN SULFATE AT 127.5°

2.5 N Sulfuric Acid

Time, hours	0.5	0.75	1.0	1.25	1.5	1.75	2.0	6.5
Amino N per g. of casein, mg.	47.2	54.5	58.8	62.0	65.2	67.0	76.2	91.4
Hydrolysis, %	50.2	57.6	62.2	65.5	69.0	71.8	80.5	96.7
K, 2d order const. × 10^3	20	18	17	15	15	15	20	...

$k/4a_{\pm} = 0.023$. Average of constants $= 17 \times 10^{-3}$.

---

[5] D. D. Van Slyke, *J. Biol. Chem.*, 12, 275 (1912).

TABLE II *(Concluded)*

1.0 N Sulfuric Acid

Time, hours	0.5	0.75	1.0	1.25	1.5	1.75	2.0
Amino N per g. of casein, mg.	30.0	37.5	43.8	49.4	52.6	55.1	58.2
Hydrolysis, %	31.8	39.7	46.3	52.2	55.6	58.2	61.5
K, 2d order const. $\times 10^{3}$	9.4[a]	8.8	8.6	8.7	8.2	8.0	8.0

[a] Value not used in obtaining average.

$k/4a_{\pm} = 0.023$. Average of constants $= 8.4 \times 10^{-3}$.

0.5 *N* Sulfuric Acid

Time, hours	0.5	0.75	1.0	1.25	1.5	1.75	2.0
Amino N per g. of casein, mg.	16.9	23.2	28.8	33.2	40.0	45.7	49.4
Hydrolysis, %	17.8	24.5	30.4	35.0	42.3	48.3	52.2
K, 2d order const. $\times 10^{3}$	4.3	4.3	4.4	4.3	4.9	5.3	5.4

$k/4a_{\pm} = 0.021$. Average of constants $= 4.7 \times 10^{-3}$.

TABLE III

THE HYDROLYSIS OF CASEIN BY HYDROGEN PHOSPHATE AT 127.5°

2.5 **N** Phosphoric Acid

Time, hours	0.5	0.75	1 .	1.25	1.5	1.75	2.0
Amino N per g. of casein, mg.	16.3	19.4	24.4	26.2	27.5	31.2	33.8
Hydrolysis, %	17.2	20.5	25.8	27.8	29.1	33.1	35.7
K, 2d order const. $\times 10^{3}$	4.2[a]	3.4	3.5	3.1	2.7	2.8	2.8

$k/a_{\pm} = 0.024$. Average of constants $= 3 \times 10^{-3}$.

3.0 N Phosphoric Acid

Time, hours	0.5	0.75	1.0	1.23	1.5	1.75	2.0
Amino N per g. of casein, mg.	18.1	21.9	23.1	25.0	2 8	30.7	35.7
Hydrolysis, %	19.2	23.2	24.5	26.4	30.4	32.5	37.7
K, 2d order const. $\times 10^{3}$	4.7[a]	4.0	3.3	2.0	2.9	2.8	3.0

[a] Value not used in obtaining average.

$k/a_{\pm} = 0.023$. Average of constants $= 3.2 \times 10^{-3}$.

TABLE IV

THE HYDROLYSIS OF CASEIN BY ACID AT 117.5°

1.0 *N* Hydrochloric Acid

Time, hours	0.5	0.75	1.0	1.23	1.5	2.0
Amino N per g. of casein, mg.	24.4	32.5	38.8	41.9	46.3	52.5
Hydrolysis, %	25.8	34.4	41.0	44.3	48.9	55.5
K, 2d order const. $\times 10^{3}$	7.0	7.0	7.0	6.4	6.2	6.2

$k/a_{\pm} = 0.0080$. Average of constants $= 6.6 \times 10^{-3}$.

Time, hours	0.5	1.0	1.5	2.0	2.5
Amino N per g. of casein, mg.	25.0	38.8	51.8	56.2	60.4
Hydrolysis, %	26.4	41.0	54.8	59.4	63.4
K, 2d order const. $\times 10^{3}$	7.2	7.0	8.1	7.3	7.0

$k/a_{\pm} = 0.0089$. Average of constants $= 7.3 \times 10^{-3}$.

TABLE IV (Concluded)

1.0 N Sulfuric Acid

Time, hours	0.5	1.0	1.5	2.0	2.5
Amino N per g. of casein, mg.	16.9	26.3	33.8	38.8	44.4
Hydrolysis, %	17.9	27.8	35.7	41.0	46.9
K, 2d order const. × 10^3	4.4[a]	3.9	3.7	3.5	3.5

[a] Value not used in obtaining average.

$k/4a_{\pm} = 0.010$. Average of constants = 3.6×10^{-3}.

TABLE V

HYDROLYSIS OF CASEIN BY ACID AT 105.5°

1.0 N Hydrochloric Acid

Time, hours	1	1.5	2.0	2.5	3.0
Amino N per g. of casein, mg.	25.0	32.6	38.2	43.8	46.3
Hydrolysis, %	26.4	34.4	40.3	46.2	48.9
K, 2d order constant × 10^3	3.6	3.5	3.4	3.5	3.2

$k/a_{\pm} = 0.0041$. Average of constants = 3.4×10^{-3}.

1.0 N Sulfuric Acid

Time, hours	1	1.5	2.0	2.5	3.0
Amino N per g. of casein, mg.	13.7	19.4	24.4	28.1	31.3
Hydrolysis, %	14.6	20.5	25.8	29.7	33.1
K, 2d order constant × 10^3	1.70	1.72	1.74	1.69	1.65

$k/4a_{\pm} = 0.0048$. Average of constants = 1.7×10^{-3}.

Discussion

Order of the Reaction.—The constants of the order of the reactions are calculated, as in the former paper,[1] on the basis of the percentage of hydrolysis according to the formula

$$K = \frac{1}{t} \times \frac{X}{100 - x} \times \frac{1}{100} \qquad (1)$$

in which x represents the percentage of protein hydrolyzed in time t. The constants calculated according to this formula are in fair agreement with each other for each experimental condition of temperature and acid concentration. The reproducibility that can be expected for these experiments is shown in Table IV, in which are given the results of two experiments at the same temperature and acid concentration carried out at different times. The average results of the calculated constants of the two experiments agree within 10% of each other.

That the experimental results best fit the equation for a second order reaction is shown in Table I, in the experiment with 1.0 N hydrogen chloride. In the tabulated results for this experiment there are given the reaction constants as calculated for a first, second and third order reaction. It is to be seen that the first order constants regularly decrease in magnitude with time, while the constants for a third order reaction regularly increase in magnitude. This, in conjunction with the agreement of the second order constants, strongly favors the viewpoint that the hydrolysis of casein, as well as of gelatin, silk fibroin and wheat gliadin follows a second order reaction.

Catalysis by Acids.—In agreement with the previous results, the catalytic effect of acids on the hydrolysis of casein has been found to be proportional to the thermodynamic activity of the acids. The velocity constants at unit activity which are given at the foot of each column of velocity constants show good agreement among themselves at each temperature. In making the calculations, the values for the activity coefficients of hydrogen chloride and sulfate were taken from the tables of Lewis and Randall.[6] As a more rigid test of this relationship, two experiments were made using the comparatively weak acid, phosphoric. The unit activity constants obtained are in good agreement with those of sulfuric and hydrochloric acids. As we found no available data for activity coefficients of phosphoric acid in the concentrations employed, measurements of the hydrogen-ion activity of the solutions were made on the hydrogen electrode, using a 0.1 molal calomel hydrogen electrode and bridging across with a saturated KCl bridge. These measurements gave an activity of 0.137 molal for the 3.0 N and 0.123 molal for the 2.5 N acids.

Effect of Temperature.—As in the previous work[1] the mathematical relationship for the change of velocity constants with temperature was determined and the equation obtained by the same procedure as previously described is

$$\log \mathrm{Ka} = 0.0307T - 5.61 \tag{2}$$

in which Ka is the reaction rate constant at unit activity and the temperature T is in degrees centigrade. This gives the means of predicting the course of casein hydrolysis at a given temperature and acid of known activity. The constant, Ka, at any temperature can be obtained from Equation 2. This multiplied by the activity of the acid used gives the velocity constant for that particular acid concentration. The time required to effect a given degree of hydrolysis can be calculated by the use of Equation 1.

Summary

1. The rate of hydrolysis of casein by acids as measured by the increase in amino nitrogen has been found to conform to the equation for a second order reaction.

2. As was previously found for other proteins, the catalytic effect of acids on casein hydrolysis is proportional to the hydrogen-ion activity of the acids.

---

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Company, New York, 1923, pp. 336, 357.

3. A quantitative relationship has been derived for the change of the rate of hydrolysis with temperature.

BERKELEY, CAWRORNIA

[CONTRIBUTION FROM THE 2. STATE UNIVERSITY, MOSCOW]

THE MECHANISM OF FORMATION OF BETA-ARYL-BETA-AMINO FATTY ACIDS BY THE CONDENSATION OF AROMATIC ALDEHYDES WITH MALONIC ACID AND ITS DERIVATIVES[1]

BY W. M. RODIONOW AND E. A. POSTOVSKAJA

RECEIVED OCTOBER 11, 1928 PUBLISHED MARCH 6, 1929

In our former investigations[2] we have found that the mechanism of Knoevenagel's synthesis of cinnamic acids[3] in the presence of ammonia is much more complicated than Knoevenagel himself and other authors assumed. We have discovered that besides cinnamic acid derivatives the corresponding amino acid is formed with a good yield, in accordance with the following equation

$$RCHO + NH_3 + CH_2(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2 + H_2O$$

By replacing malonic acid by its esters, A. M. Fedorova[2b] obtained the esters of β-aryl-β-amino-isosuccinic acid

$$RCHO + NH_3 + CH_2(COOC_2H_5)_2 = RCH(NH_2)CH(COOC_2H_5)_2 + H_2O$$

After saponification with hydrochloric acid these derivatives give, quantitatively, the corresponding amino acids.

Two possibilities may be worthy of consideration in order to interpret the mechanism of this reaction

I (a) $RCHO + NH3 = RCH(OH)NH_2$
(b) $RCH(OH)NH_2 + CH_2(COOH)_2 = RCH(NH_2)CH(COOH)_2 + H_2O$
(c) $RCHNH_2CH(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2$
11 (a) $RCHO + CH_2(COOH)_2 = RCH{=}CHCOOH + CO_2 + H_2O$
(The final result of Knoevenagel's reaction)
(b) $RCH{=}CHCOOH + NH3 = RCHNH_2CH_2COOH$

In favor of the second explanation and against the first may be cited the interesting investigations of Korner and Menozzi,[4] Engel[5] and of

---

[1] This paper is an abstract of a thesis presented by E. A. Postovskaja in partial fulfilment of the requirements for the degree of Diplom-chemist of the 2. State University of Moscow.

[2] (a) W. M. Rodionow and E. Th. Malevinskaja, *Ber.*, 59, 2952 (1926); (b) W. M. Rodionow and A. M. Fedorova, *ibid.*, **60**, 804 (1927); (c) *Arch. Pharm.*, 266, 116–311 (1928).

[3] Knoevenagel, *Ber.*, 31, 2596 (1898).

[4] Korner and Menozzi, *Ber.*, 21, ref. 86 (1886); *ibid.*, **22**, ref. 735 (1889); *ibid.*, 27, ref. 121 (1894).

[5] Engel, Compt. *rend.*, 104, 1805 (1887); 106, 1677 (1888).

many other authors, who have found that a certain yield of β-amino acids may be prepared by treatment of esters of unsaturated acids with ammonia.

The execution of this reaction is very difficult; it is necessary to warm both components many hours, often many days, under pressure in sealed tubes or in an autoclave. The yields are most unsatisfactory, only Engel having asserted that he obtained excellent yields in his preparations.

The formation of arylamino fatty acids in our case, especially with non-substituted malonic acid, goes very easily at moderate temperature not exceeding 90°, and generally under ordinary pressure. All the conditions of this reaction make the first explanation more probable and it seems that the first consideration is more nearly correct and corresponds better to all the facts.

In order to confirm this supposition, we have made our aldehyde condensations with mono-substituted malonic esters of the general formula $R'CH(COOC_2H_5)_2$, where R′ represents any aliphatic or fatty aromatic radical.

Substances of this type cannot give condensations with loss of water and formation of unsaturated acids capable of additional reactions with ammonia. It may also be mentioned that according to the researches of Claisen[6] the mono-substituted malonic acids in general do not condense with aldehydes.

We have carried out our condensations with methyl-, ethyl- and benzylmalonic esters. Benzaldehyde and piperonal were employed as second components.

It has already been mentioned that this condensation takes place under ordinary pressure, but with substituted malonic esters the yield increases generally, when the reaction is carried out in sealed tubes; but for this increase it is of much greater importance to have the correct temperature and particularly the correct time of heating.

In most cases the portion of the materials used which does not enter into the reaction remains unchanged; sometimes this condensation is contaminated with the formation of such by-products as diamides of the general formula $RCH(CONH_2)_2$, but we could never find any unsaturated compounds, which affirms the correctness of the first explanation of the mechanism of this interesting reaction.

We have extended our investigations to free methyl-, ethyl- and benzylmalonic acids and obtained the corresponding amino acids. It is evident that in this case the reaction takes more complicated paths, and as final substances the amino-*mono*-carbonic acids are formed according to the following equation

$$RCHO + R'CH(COOH)_2 + NH_3 = RCH(NH_2)CH(R')COOH + H_2O + CO_2$$

---

[6] Claisen and Crimson, *Ann.*, **218, 144 (1883)**.

The β-aryl-β-amino-α-alkylpropionic acid obtained is identical with the acid that can by prepared by saponification of the corresponding ester, $RCHNH_2C(R')(COOC_2H_5)_2$; R and R' must naturally be identical in ester and in acid.

The identity of both acids affirms again the correctness of our supposition. This is very important to note, since the use of free mono-substituted malonic acids makes possible many kinds of reaction and besides β-amino acids there also may be formed unsaturated substances, the constitutions of which have not yet been elucidated completely.

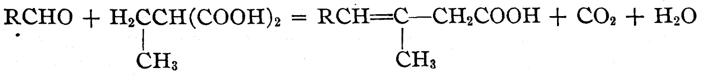
The formation of unsaturated acids may be explained in the following manner

$$\text{I}\quad RCHO + CH_3CH(COOH)_2 = RCH{=}CHCH_2COOH + CO_2 + H_2O$$

$$\text{II}\quad (a)\quad RCHO + CH_3CH(COOH)_2 = RCH(OH)CH(CH_3)(COOH)_2$$

$$(b)\quad RCH(OH)CH(CH_3)(COOH)_2 = RCH{=}C(CH_3)COOH + H_2O + CO_2$$

When a more complicated mono-substituted malonic acid is employed, that is, ethylmalonic acid, a third isomeride may be expected, as the possibility of an aldehyde condensation with the methyl group or with the methylene group of the ethyl radical is not excluded



$$RCHO + \underset{\displaystyle CH_3}{H_2\underset{|}{C}}CH(COOH)_2 = RCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2COOH + CO_2 + H_2O$$

If the formation of amino acids may be ascribed to the addition of ammonia to the double linkage of unsaturated acids, we should expect in this case, in accordance with the investigations of Koerner, Menozzi, Engel and others, to obtain a-amino acids but our investigations show that this supposition is not justified.

The preparation of p-amino esters is a very simple operation. Equimolecular proportions of aromatic aldehyde, mono-substituted malonic esters and a little excess of alcoholic ammonia solution are heated on a water- or oil-bath until the alcohol is evaporated; the dry mixture is heated for three to four hours and then dissolved in ether and shaken with sodium bisulfite solution to remove any residue of unreacted aldehyde; the etheric solution is washed with water, dried with sodium sulfate and then treated with dry hydrogen chloride. The hydrochloride of the β-amino-ester separates as a heavy oil that solidifies not too rapidly and crystallizes from alcohol usually in snow-white needles. It is very easy to fix the end-point of the reaction with mono-substituted malonic acids. The mixture is heated until the development of carbon dioxide ceases. The *dry* residue is dissolved with addition of sodium carbonate in warm water (*ca.* 60°) and treated with ether in order to remove the unreacted aldehyde; the water solution is acidified with hydrochloric acid and the precipitated unsaturated acid is filtered off by suction and washed with water; the filtrate is shaken with ether to free it from unsaturated and fatty acids and then evaporated on the water-bath; it is finally dried in a desiccator over sulfuric acid in *vacuo.*

The resulting mixture, containing chlorohydrate of β-amino acid, common salt and ammonium chloride, is dissolved in absolute alcohol, filtered by suction from inorganic salts and evaporated on the water-bath. The chlorohydrate of the amino acid nevertheless usually is contaminated with small quantities of inorganic salts and must be twice recrystallized from absolute alcohol. The product is now pure and gives correct analytical results.

Experimental Part

Diethyl β-Phenyl-β-amino-α-methyl-ethane-α,α-dicarbonate Hydrochloride, C_6H_5-$CH(NH_2HCl)C(CH_3)(COOC_2H_5)_2$.—In a little, round-bottomed flask fitted with a direct condenser are placed 5 g. of methylmalonic ester, 3 g. of benzaldehyde and 1 g, of alcoholic ammonia solution (12 g. of ammonia in 100 g. of dry alcohol). After evaporating off the alcohol, the mixture is heated on a water-bath for five hours and then dissolved in 100 cc. of dry ether. Dry hydrogen chloride is then passed into the solution. The hydrochloride separates as a heavy oil. The flask is then tightly stoppered and allowed to stand until the oil sets to a mass of crystals, which usually requires one or two days. Double crystallization from hot, dry alcohol gives colorless needles, m. p. 158°; yield, 1.5 g. (about 16%).

A much better yield is obtained with modified conditions, as follows: 10 g. of methylmalonic ester, 6 g. of benzaldehyde and 15 cc. of alcoholic ammonia solution (10 g. of ammonia in 100 g. of alcohol) were heated in a sealed tube on a strongly boiling water-bath for seven hours. The mixture was then placed in a round-bottomed flask, the alcohol distilled off, the residue dissolved in dry ether, filtered from 0.6 g. of methylmalonyldiamide (m. p. 203") and the hydrochloride of the amino ester precipitated from the filtrate with hydrogen chloride. The product was crystallized from alcohol and dried in a desiccator. 2.8 g. of benzaldehyde and 4.6 g. of methylmalonic acid were recovered from the ethereal solution after filtering off the amino ester. The yield of the ester, calculated on the benzaldehyde actually combined, then increases to 96.6%.

Hydrochloride of Diethyl β-Piperonyl-β-amino-α-methyl-ethane-α,α-dicarboxylate, $CH_2O_2C_6H_3CH(NH_2HCl)C(CH_3)(COOC_2H_5)_2$.—Five g. of diethyl methylmalonate, 4.3 g. of piperonal and 20 cc. of 7% alcoholic ammonia solution were placed in a sealed tube and heated at 150° for five hours on an oil-bath. The mixture was evaporated to dryness, dissolved in dry ether and treated exactly as in the preceding preparation. The oil which separates solidifies very slowly and after several crystallizations the pure substance forms large plain needles. The ethereal solution from which the amino ester has been removed contains only unchanged piperonal and diethyl methylmalonate.

Hydrochloride of Diethyl β-Phenyl-β-amino-α-ethyl-ethane-α,α-dicarboxylate, $C_6H_5CH(NH_2HCl)C(C_2H_5)(COOC_2H_5)_2$.—Five g. of diethyl ethylmalonate, 2.8 g. of benzaldehyde and 1 g. of 12% alcoholic ammonia solution were heated in a sealed tube for five hours on a water-bath The alcohol was then evaporated, leaving in the flask a heavy oil. The oil was dissolved in 100 cc. of ether and filtered from 0.5 g. of an unknown substance, insoluble in ether, which was probably the diamide of ethylmalonic acid (m. p. 199°). The filtrate was treated with dry hydrogen chloride and an oil separated which solidified to fine, white needles. It was crystallized twice from alcohol. The best way of purifying the hydrochloride is by solution in alcohol and precipitation with dry ether. The ethereal alcoholic solution contains unchanged benzaldehyde

(1 **g.)**, diethyl ethylmalonate *(1.8* **g.**) and in small and varying quantities an unidentified substance melting at **74°.**

Hydrochloride of Diethyl **β-Piperonyl-β-amino-α-ethyl-ethane-α,α-dicarboxylate,** $CH_2O_2C_6H_3CH(NH_2HCl)C(C_2H_5)(COOC_2H_5)_2$.—Ten g. of diethyl ethylmalonate, 8 g. of piperonal and *20* cc. of 10% alcoholic ammonia solution were heated at 130–140° in a sealed tube for ten hours, with subsequent treatment as in the previous experiment. The **very** small yield of amino ester is explainable by the stability of the condensation product of piperonal with ammonia. The ester is insoluble in ether and may be isolated very easily.

Hydrochloride of p–Phenyl–8–amino–a–methylpropionic Acid, $C_6H_5CH(NH_2HCl)$-$CH(CH_3)COOH$.—**Five** g. of methylmalonic acid, *4.5* g. of benzaldehyde and *15* cc. of 10% alcoholic ammonia solution were heated on a water-bath until the evolution of carbon dioxide had ceased. The residue was dissolved in *20* g. of 15% soda solution at **60°.** The undissolved oil was extracted with ether *(0.2* g.). The alkaline solution was acidified with hydrochloric acid and again extracted with ether. This extract contains an unsaturated, nitrogen-free acid. After crystallization from alcohol it melted at 173° with decomposition. The water solution after treatment with ether was evaporated to dryness. The resulting hydrochloride of phenylaminomethylpropionic acid is contaminated with inorganic salts and must be crystallized from absolute alcohol.

Hydrochloride of **β-Piperonyl-β-amino-α-methylpropionic** Acid, $CH_2O_2C_6H_3CH$-$(NH_2HCl)CH(CH_3)COOH$.—Three and one-half g. of methylmalonic acid, *4.5* g. of piperonal and *15* cc. of 10% **alcoholic** ammonia solution were heated for six days on a water-bath until the evolution of carbon dioxide ceased. The residue was dissolved in *15* cc. of 15% soda solution and further treated as in the previous preparation. The first ethereal extract gave *0.9* g. of oil. The yield of unsaturated acid melting at 201–202° was only *0.8* g., about *13%* of the theoretical. It is either $CH_2O_2C_6H_3CH{=}CH$-CH_2COOH or $CH_2O_2C_6H_3CH{=}C(CH_3)COOH$. A molecular weight determination on the unsaturated acid gave *202.4;* calcd. for $C_{10}H_9O_4$, 206.

Hydrochloride of **β-Phenyl-β-amino-α-ethylpropionic** Acid, $C_6H_5CH(NH_2HCl)$-$CH(C_2H_5)COOH$.—Nine g. of **ethylmalonic** acid, *7.2* g. of benzaldehyde and 30 cc. of *10%* alcoholic ammonia solution were heated for five hours on a water-bath and then for three hours at **145°.** The mixture was dissolved in *30* cc. of 15% soda solution and

TABLE I

ANALYTICAL AND OTHER DATA OF ACID HYDROCHLORIDES

Diethyl β-( )-β-amino-a-( )-ethanedicarboxylates	**Yield, g.**	**Yield, %**	**M. p., °C.**	**Formula**	**Analyses Calcd. Cl, %**	**Analyses Calcd. N, %**	**Analyses Pound Cl, %**	**Analyses Pound N, %**
Phenyl, methyl	*9.2*	*51.7*	*158*	$C_{15}H_{22}O_4NCl$	11.20	4.43	11.17	4.51
Piperonyl, methyl	*3.9*	*38.2*	125–127	$C_{16}H_{22}O_6NCl$	9.86	3.89	·9.72	4.13
Phenyl, ethyl	*1.5*	*17.0*	*166*	$C_{16}H_{24}O_4NCl$	10.76	4.25	10.64	4.43
Piperonyl, ethyl	1.2	*6.0*	*157*	$C_{17}H_{24}O_6NCl$	9.49	..	9.43	..
Propionic adds								
Phenyl, methyl	*5.5*	*60.4*	*225*	$C_{10}H_{14}O_2NCl$	16.45	6.5	16.32	6.55
Piperonyl, methyl	*5*	*76.95*	...	$C_{11}H_{14}O_4NCl$	13.28	5.39	13.26	5.21
Phenyl, ethyl	*3.7*	*23.7*	*249*	$C_{11}H_{16}O_2NCl$	15.45	6.1	15.39	6.29
Piperonyl, ethyl	*2.5*	*13.4*	*215"*	$C_{12}H_{16}O_4NCl$	12.92	5.12	12.76	4.94
Phenyl, benzyl	*5.2*	*34.6*	222	$C_{16}H_{18}O_2NCl$	12.17	4.80	12.05	4.96
Piperonyl, benzyl	*3.5*	*20.3*[b]	203–205[a]	$C_{17}H_{18}O_4NCl$	10.54	4.17	10.53	4.07

[a] With decomposition.

[b] 42.3 calculated on the basis of piperonal actually combined.

treated with ether. The ethereal solution gave **2.6** g. of oil (principally contaminated benzaldehyde). After acidifying with hydrochloric acid, the water solution gave **4** g. of unsaturated acid **(36%** of the theoretical) with a melting point of 107°. The hydrochloride of the amino acid was crystallized from alcohol. **A** molecular weight determination on the unsaturated acid gave **177.9;** calcd. for $C_{11}H_{12}O_2$, **176.**

Hydrochloride of β-**Piperonyl**-β-**amino**-α-**ethylpropionic** Acid.—Nine g. of ethylmalonic acid, **10.2 g.** of piperonal and **30** cc. of 10% alcoholic ammonia solution were heated for ten hours on a water-bath and then for eight hours at 145°, considerable tar being formed. Treatment with soda solution gave an oil insoluble in water, soda and ether. The water solution after acidification gave **4.3** g. (about 31% of the theoretical) of an unsaturated acid melting at 135° and, after evaporation, the amino acid, which may be crystallized from absolute alcohol. The molecular weight of the unsaturated acid was determined as **216;** calcd. for $C_{12}H_{12}O_4$, **220.**

Hydrochloride of β-**Phenyl**-β-**amino**-α-**benzylpropionic** Acid, $C_6H_5CH(NH_2HCl)$-$CH(CH_2C_6H_5)COOH$.—Ten g. of benzylmalonic acid, **5.4** g. of benzaldehyde and **20** cc. of 10% alcoholic ammonia solution were heated for one hour on a water-bath with a condenser and then for three hours at 145°. The mixture was dissolved in soda solution and treated with ether. On evaporating the ethereal solution an oil separated **(2.8 g.).**[7] The water solution was acidified with hydrochloric acid and gave 6.5 g. **(53%** of the theoretical) of an unsaturated acid, probably $C_6H_5CH{=}C(C_6H_5)CH_2COOH$, crystallizing from alcohol in snow-white needles with a melting point of **160".** After removing this substance, the water solution was shaken several times with ether, from which **0.5** g. of hydrocinnamic acid was isolated, m. p. 40° uncrystallized and 47° after crystallization. **A** mixed melting point with a known sample gave no depression. The solution was finally evaporated to dryness and the residue crystallized from alcohol. A molecular weight determination of the unsaturated acid gave **234.1;** calcd. for $C_{16}H_{14}O_2$, **238.**

Another Method of Preparation.—Five g. of benzylmalonic acid, **4** g. of benzhydramide and **20** cc. of alcohol were heated for eight hours on a water-bath and then at **120–125'** for six hours. The treatment of the mixture was carried out exactly as in the foregoing experiment and gave **1.6** g. of oil, **2.9** g. of unsaturated acid (m. p. 160–161°), **0.3** g. of hydrocinnamic acid and **3.9** g. of the hydrochloride of β-**phenyl**-β-**amino**-α-benzylpropionic acid (about 52% of the theoretical amount).

Hydrochloride of β-**Piperonyl**-β-**amino**-α-**benzylpropionic** Acid, $CH_2O_2C_6H_3CH$-$(NH_2HCl)CH(CH_2C_6H_5)COOH$.—Ten g. of benzylmalonic acid, **7.7** g. of piperonal and **30** cc. of 10% alcoholic ammonia solution were heated for twelve to thirteen hours on a water-bath. The mixture was dissolved in soda solution and filtered from **2.8** g. of crystalline material insoluble in cold soda solution (probably the diphenylaminopropane derivative), In order to remove the unchanged piperonal, the water solution was treated with benzene. The benzene solution was concentrated on a boiling water-bath to a thin sirup; crystallization usually began as soon as the sirup cooled, **4** g. of piperonal being separated in this way. The water solution was then acidified with hydrochloric acid and **2.8** g. of unsaturated acid melting at 205° separated. This yield was about 20% of the theoretical calculated for $CH_2O{=}C_6H_5CH{=}C(C_6H_5)CH_2COOH$. The acid solution was extracted with ether and gave **2.3** g. of unchanged benzylmalonic acid. Finally, the water solution was evaporated on the water-bath and the residual hydrochloride was crystallized from alcohol. **A** molecular weight determination of the unsaturated acid gave **284.9;** calcd. for $C_{17}H_{14}O_4$, **282.**

---

[7] The investigation of this substance has not been finished but it seems to he α,γ-diphenyl-α-aminopropane, $C_6H_5CH(NH_2)CH_2CH_2C_6H_5$.

Summary

The mechanism of formation of β-aryl-β-amino acids is explained; a general method of preparation of the diethyl esters of β-aryl-β-amino-α-alkyl-ethane-α,α-dicarbonic acids and also of the preparation of β-aryl-β-amino-α-alkylpropionic acids is worked out and many examples of this class of compound are described.

Moscow, Russia

[Contribution from the Technical College, Moscow]

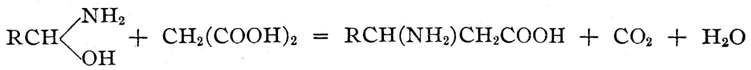
SYNTHESIS OF BETA-ARYL-BETA-AMINO-ETHANE-ALPHA, ALPHA-DICARBONIC ACIDS

THE MECHANISM OF KNOEVENAGEL'S SYNTHESIS OF CINNAMIC ACIDS

By W. M. Rodionow

Received October 11, 1928 Published March 6, 1929

For some time the writer and his collaborators[1] have studied Knoevenagel's synthesis of cinnamic acids[2] and have found that this reaction, in the presence of alcoholic ammonia solution as a catalytic agent, takes a more complicated path than is generally assumed. We have proved that in this reaction besides cinnamic acid derivatives β-aryl-β-aminopropionic acids also are formed in accordance with the following equation



$$RCH\begin{matrix}\diagup NH_2\\ \diagdown OH\end{matrix} + CH_2(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2 + H_2O$$

In our paper with E. A. Postovskaja[3] we gave a satisfactory explanation of the mechanism of this reaction and could show that the formation of aryl-β-aminopropionic acids is a condensation reaction between aldehyde-ammonia and malonic acid and not an addition reaction of ammonia to the double bond of the corresponding cinnamic acid.

In our fundamental experiments we have first taken as condensing agent only alcoholic ammonia solution but later, with Mrs. Malevinskaja and Miss V. B. Zenkovich,[4] we replaced the ammonia with monomethylamine and monoethylamine and thus prepared with fair yields β-aryl-β-alkylaminopropionic acids

$$RCHO + NH_2R' + CH_2(COOH)_2 = RCHNHR'CH_2COOH + H_2O + CO_2$$

R' may be either methyl or ethyl.

We also tried to prepare β-aryl-β-dialkylaminopropionic acids and found that in this case the cinnamic acid derivatives are formed nearly

---

[1] W. M. Rodionow and E. Th. Malevinskaja, *Ber.*, 59, 2952 (1926); W. M. Rodionow and A. M. Fedorova, *ibid.*, 60, 804 (1927); *Arch. Pharm.*, 266, 126–311 (1928).

[2] Knoevenagel, *Ber.*, 31, 2596 (1898).

[3] W. M. Rodionow and E. A. Postovskaja, This Journal, 51, 841 (1929).

[4] The unpublished thesis of Miss V. B. Zenkovich from the Laboratory for Alcaloid-Chemistry of the 2. State University of Moscow.

exclusively, accompanied by very small amounts of dialkylaminopropionic acids. We extended our preparations to other amines, especially to piperidine, which is, according to the investigations of many authors, the best catalytic agent for the synthesis of cinnamic acid, and we can state that in this case only cinnamic acids are formed and no traces of β-aryl-8-piperidylpropionic acids can be isolated.

This failure to prepare the piperidyl derivatives has induced us to modify the conditions of our condensations and we carried out this reaction at room temperature. Indications toward such modification had already been given in the very interesting paper of Mannich and Ganz.[5] These authors found that β-aminodicarbonic acids are formed when monosubstituted malonic acids, ammonia, or better still, methylamine or dimethylamine and formaldehyde are mixed together and allowed to stand at ordinary temperature or in ice. After ten to twenty hours a solid mass of crystals separates from the mixture and the corresponding aminodicarbonic acids are formed.

With Miss Holmogorzeva[6] we have worked out a method of preparation of such aryl-β-piperidylethane dicarbonic acids. It is very simple and consists in mixing piperidine and malonic acid at ordinary temperature in an alcoholic solution of the aromatic aldehyde. In the case of benzaldehyde the following reaction takes place

$$C_6H_5CHO + C_5H_{11}N + CH_2(COOH)_2 = C_6H_5CH(NC_5H_{10})CH(COOH)_2 + H_2O$$

and β-phenyl-β-piperidylethane-α,α-dicarbonic acid is formed (details in Experimental Part).

The replacement of benzaldehyde with piperonal gives with a good yield β-piperonyl-β-piperidylethanedicarbonic acid. The attempts to obtain β-aryl-β-amino-ethanedicarbonic acids were also crowned with success when an equimolecular mixture of benzaldehyde, malonic acid and a small excess of alcoholic ammonia solution was allowed to stand for some time. After five to ten minutes a reaction occurred with evolution of heat and on cooling the phenylamino-ethanedicarbonic acid separated as a white crystalline mass.

All compounds thus obtained are stable at ordinary temperature and may even be crystallized from alcohol and water, but on heating (above the melting or decomposition point) these substances undergo a decomposition with evolution of carbon dioxide and sometimes of ammonia.

It was proved further without difficulty that the heating of β-aryl-β-piperidylethanedicarbonic acids gives exclusively the corresponding cinnamic acid, but aryl-β-amino-ethanedicarbonic acids furnish a mixture of cinnamic acid and aryl-β-alanine.

---

[5] Mannich and Ganz, *Ber.*, 55, 3487 (1922).

[6] The unpublished thesis of Miss J. A. Holmogorzeva from the Laboratory for Alcaloid-Chemistry of the 2. State University of Moscow.

Further attempts were made in order to obtain β-alkylated β-aryl-β-amino-ethanedicarbonic acids. Two experiments, carried out by Miss Zenkovich, with alcoholic ethylamine solution proved that such condensations are possible, also with a fair yield, and two compounds of this type, β-piperonyl-β-ethylamino-ethanedicarbonic acid and β-phenyl-β-ethylamino-ethanedicarbonic acid are described in the Experimental Part.

It has already been mentioned that these condensations give an excellent yield (80–90% and more of the theoretical amount); but as the formation of β-aryl-aminopropionic acid is always accompanied by cinnamic acid and the maximum yield of either component seldom reaches 50%, it may be assumed that Knoevenagel's synthesis of cinnamic acid is a secondary process: first the formation of arylamino-ethanedicarbonic acid takes place and, second, this compound being unstable on heating, decomposes with evolution of carbon dioxide and ammonia and forms cinnamic acid.

The condensation of malonic acid with amine and aromatic aldehyde occurs then at room temperature or, better, on slight cooling, in the following way

$$RCHO + NH_3 + CH_2(COOH)_2 = RCHNH_2CH(COOH)_2 + H_2O$$

This compound may be isolated with an excellent yield; generally this process is not stopped at this point but the product is warmed further and the arylamino-ethanedicarbonic acid produced decomposes in two directions

$$RCH(NH_2)CH(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2 \qquad (1)$$

$$RCH(NH_2)CH(COOH)_2 = RCH{=}CHCOOH + CO_2 + NH_3 \qquad (2)$$

The same products also may be obtained either by heating the isolated arylamino-ethanedicarbonic acid above its melting point or by dissolving it in hot water and acidifying with strong mineral acid.

The proportion of the mixture of both acids may be changed by many means: temperature, concentration of mineral acid, the nature of it and many other circumstances have a great influence on the course of this reaction and on the yield of each component.

It is interesting to note that β-aryl-β-amino-ethanedicarbonic acids readily undergo decomposition on heating and on boiling with mineral acids. The aryl-β-aminopropionic acids are more stable but in many cases the warming of their hydrochlorides with sodium acetate also causes elimination of the ammonia molecule and a corresponding cinnamic acid is formed with a fair yield. Another observation which was made is that the condensation with veratric aldehyde does not at ordinary temperatures give the dimethoxrphenylamino-ethanedicarbonic acid. Many attempts in this direction resulted only in the isolation of uninviting, resinous, tarry compounds from which with great difficulty were recovered the dimethoxycinnamic acids (probably a mixture of cis and *trans* isomerides).

Nearly all condensations with piperonal occur with a poorer yield than the same ones with benzaldehyde.

On summarizing all observations described in this paper and in our former investigations, the conclusion may be drawn that not only β-aryl-β-amino-ethanedicarbonic acids but also β-aryl-β-aminomonocarbonic acids are not so stable as the well-known a-amino acids. The existence of methoxy groups and also of methylene-dioxy groups in the benzene ring makes these compounds much more unstable, as was proved by unsuccessful attempts to obtain the dimethoxyphenylamino-ethanedicarbonic acid and smaller yields in many condensations with piperonal.

This work, as a whole, raises an interesting question from the biochemical standpoint. It is not impossible that the protein molecule contains not only a-amino acids but in certain, though indeed very small amounts, also β-amino acids; our methods for their isolation are too crude and the acid hydrolysis at comparatively high temperature decomposes β-amino compounds and leaves unchanged only the more stable a-amino acids.

The same decomposition can take place in living nature, where several enzymes can undertake the role of heat and transform β-amino acids and especially methoxylated compounds into cinnamic acid derivatives, and in this manner may be explained the fact that in many plant oils and drugs are found such acids as ferulic, isoferulic, coffeinic and many other styrolene derivatives.

Experimental Part

This part of the work was carried out by Miss V. B. Zenkovich and Miss J. A. Holmogorzeva; their shares are indicated with their initials (Z. or H.) at each preparation. For many of the analyses and constant assistance I am much indebted to Miss A. M. Fedorova (F.), to whom I also express my thanks in this place.

β-Piperonyl-β-ethylaminopropionic Acid (Z.), $CH_2O_2C_6H_3CH(NHC_2H_5)CH_2COOH$.—A mixture of 22 g. of piperonal, 70 cc. of 11% alcoholic ethylamine solution and 18 g. of malonic acid was heated on a boiling water-bath with the condenser set for distillation. The alcohol was distilled off and the yellowish residue dissolved in hot water and acidified with an excess of acetic acid. On cooling, the piperonylacrylic acid separated nearly quantitatively and was filtered off; 19.6 g. (70% of the theoretical). The filtrate was evaporated to dryness and crystallized from alcohol. The piperonylethylaminopropionic acid is insoluble in ether, sparingly soluble in alcohol and easily soluble in water, from which it crystallizes in fine, white needles.

The **nitrosamine** of this acid, $CH_2O_2C_6H_3CH(NNOC_2H_5)CH_2COOH$, may be prepared easily by treating the hydrochloride of the acid with sodium nitrite solution. It crystallizes very well from water and forms long, fine needles which melt at 136–138°.

Hydrochloride of β-Piperonyl-β-dimethylaminopropionic Acid (Z.), $CH_2O_2C_6H_3CH$-

$[N(CH_3)_2HCl]CH_2COOH$.—Twenty g. of piperonal, 40 cc. of 18% alcoholic dimethylamine solution and 16 g. of malonic acid were heated on a strongly boiling water-bath. After an hour 10 cc. of dimethylamine solution of the same strength was added and the whole warmed until the evolution of carbon dioxide ceased (nine to ten hours). The residue was dissolved in hot water, acidified with hydrochloric acid and the piperonylacrylic acid filtered off and dried; yield 14 g. (about 95% of the theoretical). The filtrate was evaporated to dryness, washed with chloroform and crystallized from alcohol. The acid has no melting point but seems to be chemically pure, as proved by its analysis.

All attempts to prepare in a similar manner the diethylamine compound were unsuccessful and only piperonylacrylic acid was obtained, in nearly quantitative yield.

β-Phenyl-β-amino-ethane-α,α-dicarbonic Acid (F.), $C_6H_5CH(NH_2)CH(COOH)_2$.—Twenty g. of benzaldehyde, 55 cc. of 6% alcoholic ammonia solution and 20 g. of malonic acid are mixed. The reaction occurs instantaneously; in order to prevent the raising of temperature the mixture is allowed to stand for twelve hours in ice water and then the solid is filtered off and washed with ether. The acid is sparingly soluble in cold water and alcohol and insoluble in ether. It crystallizes from alcohol in long lustrous needles.

On heating at 150° the acid decomposes with evolution of carbonic acid and ammonia and gives exclusively cinnamic acid; but on heating with hydrochloric acid 5 g. of the acid gave 2.50 g. of the hydrochloride of β-phenylalanine (ca. 50% of theoretical amount) and 1.65 g. of cinnamic acid (ca. 40%). The loss of the last compound is only to be explained with its volatility.

β-Phenyl-β-piperidylethane-α,α-dicarbonic Acid (F. and H.), $C_6H_5CH(NC_5H_{10})CH(COOH)_2$.—Four and nine-tenths g. of malonic acid was dissolved in 20 cc. of alcohol, 5 g. of benzene added and then 4 g. of piperidine. The reaction occurs with great evolution of heat and a white, crystalline mass begins to separate almost immediately. The mixture was allowed to stand for twelve hours and then the solid was filtered off and crystallized from alcohol. The acid is easily soluble in hot water, sparingly soluble in cold water and alcohol and insoluble in ether. It crystallizes from alcohol in lustrous plates and from water in long needles It is interesting to observe that only one carboxylic group of this acid is neutralized by alkali. Calcd. for one carboxyl group of 0.1 g. of acid: 3.6 cc. of 0.1 N sodium hydroxide. Found: 3.5.

Five grams of the acid was heated with water and hydrochloric acid; on cooling, 2.2 g. of cinnamic acid (m. p. 132–134°) separated (84.6% of the theoretical). From the filtrate were recovered the whole amount of piperidine and small amounts of cinnamic acid; no traces of β-phenyl-β-piperidylpropionic acid were found.

β-Piperonyl-β-piperidylethane-α,α-dicarbonic Acid (H.), $CH_2O_2C_6H_3CH(NC_5H_{10})CH(COOH)_2$.—Four and three-tenths g. of piperonal, 3 g. of malonic acid and 2.3 g. of piperidine were dissolved in 15 cc. of absolute alcohol and allowed to stand for twenty-four hours. The compound which separated off was crystallized from alcohol, giving lustrous plates. The acid is easily soluble in water, sparingly soluble in alcohol and insoluble in ether. Only one carboxyl group reacts with sodium hydroxide.

β-Phenyl-β-ethylamino-ethane-α,α-dicarbonic Acid (Z.), $C_6H_5CH(NHC_2H_5)CH(COOH)_2$.—Four and one-half g. of benzaldehyde, 13 cc. of 15% alcoholic ethylamine solution and 4.5 g. of malonic acid are mixed; reaction occurs instantaneously, the temperature rises to 50° and after a few minutes the aminodicarbonic acid begins to separate and is filtered off. After standing for some hours a small amount more of the compound may be recovered from the filtrate. The acid may be crystallized from hot alcohol. Lack of time made impossible the repurification and re-analysis of the substance.

TABLE I

ANALYTICAL AND OTHER DATA OP THE ACIDS

β-( )-β-( )-amino-propionicacids	Yield, g.	Yield, %	M. p., °C.	Formula	Analysis, N, % Calcd.	Analysis, N, % Found
Piperonyl, ethyl	9.4	26	198–200	$C_{12}H_{15}O_4N$	5.90	5.60
Piperonyl, **dimethyl-**[a]	1	2–3	.....	$C_{12}H_{16}O_4NCl$[a]	5.12	5.32
β-( )-β-( )-ethane-α,α-&carbonic acids						
Phenyl, amino	30.0	76	148	$C_{10}H_{11}O_4N$	6.69	6.98
Phenyl, piperidyl	11.8	91	163–164[b]	$C_{15}H_{19}O_4N$	5.05	5.07
Piperonyl, piperidyl	8	87	150–152[b]	$C_{15}H_{19}O_6N$	4.36	4.42
Phenyl, ethylamino	6	68.8	163–164[b]	$C_{12}H_{15}O_4N$	5.9	6.54
Piperonyl, ethylamino	5.8	58.2	155–157[b]	$C_{13}H_{15}O_6N$	4.98	4.94

[a] Hydrochloride. Calcd.: Cl, 12.95. Found: 13.09.

[b] With decomposition.

β-Piperonyl-β-ethylamino-ethane-α,α-dicarbonic Acid (Z.), $CH_2O_2C_6H_3CH(NHC_2H_5)CH(COOH)_2$.—Five and three-tenths g. of piperonal, 3.85 g. of malonic acid and 12 cc. of 15% alcoholic ethylamine solution were mixed and treated as in the previous experiment. The acid is easily soluble in hot water, less so in alcohol and insoluble in ether; it crystallizes from alcohol in little rods.

Summary

A new explanation of the mechanism of Knoevenagel's synthesis of cinnamic acids is proposed, a method of preparation of aryl-β-amino-ethanedicarbonic acids and their N-substituted derivatives is described and the specific preparation of some compounds of this type and the properties of these compounds are given.

MOSCOW, RUSSIA

[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

REACTION OF CHLORO-ACETIC ACIDS WITH ZINC

BY HOWARD WATERS DOUGHTY AND DONALD A. LACOSS

RECEIVED OCTOBER 13, 1928 PUBLISHED MARCH 6, 1929

In previous contributions from this Laboratory[1,2] the reaction of trichloro-acetic acid with copper has been discussed and it has been shown that it affords an excellent method for the preparation of dichloro-acetic acid. The reaction is exothermic and the acid was used in benzene solution. During these investigations it was noted that the reaction of trichloro-acetic acid with zinc is also very vigorous, and the present authors, therefore, have studied this reaction. The work has been interrupted by change of residence of the junior author, so it seems advisable to make a brief statement of results so far obtained.

When zinc dust is added to a solution of trichloro-acetic acid in benzene,

[1] Doughty and Freeman, THIS JOURNAL, 44, 636 (1922).

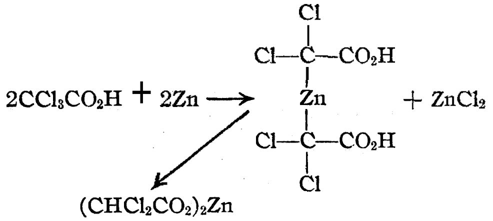
[2] Doughty and Black, *ibid.*, 47, 1091 (1925).

much heat is evolved and zinc chloride is formed, together with zinc dichloro-acetate and other products, depending on the relative quantities of acid and zinc. The reaction product is not easy to work with, owing apparently to the hygrosopic nature of the zinc chloride; the reaction was therefore studied in aqueous solution and it was found that it is not necessary to use zinc dust, as mossy zinc reacts very readily.

The least expected of the results obtained in these experiments is the fact that no hydrogen is evolved. When one mole of trichloro-acetic acid, dissolved in one liter of water, reacts with one gram atomic weight of mossy zinc, the zinc is dissolved very rapidly, the solution becomes neutral and contains zinc chloride and zinc dichloro-acetate, but no hydrogen is evolved. If more than this amount of mossy zinc is added the excess remains after the reaction is over. If zinc dust is added in excess, however, a white precipitate forms and part of the zinc dust is converted into zinc chloride. This white precipitate has not been identified. It contains zinc and is soluble in acids. The reaction of trichloro-acetic acid with mossy zinc is quantitative and the equation is

$$2CCl_3CO_2H + 2Zn = ZnCl_2 + (CHCl_2CO_2)_2Zn$$

The fact that no hydrogen is evolved in this reaction indicates that the mechanism of the reaction must be considered as similar to that of trichloro-acetic acid with copper. It has been suggested[1,2] that with copper an intermediate compound is formed in which the copper is joined directly to the carbon and that this is followed by a rearrangement in which hydrogen and copper exchange places. A similar mechanism for the reaction of trichloro-acetic acid with zinc would be expressed by the following



As in the corresponding reaction with copper, the hydrogen shifts from the labile or ionizable position in the carboxyl group to the very stable position in the dichloromethyl group. Apparently this reaction is very much more rapid than the more usual replacement of hydrogen ions by zinc ions as in the action of hydrochloric acid with zinc. The fact that a corresponding action takes place with copper and trichloro-acetic acid makes this explanation appear more probable than to assume that "nascent hydrogen" is formed which then reduces the trichloro-acetic acid to dichloro-acetic acid.

In a typical experiment, 32.8 g. (0.5 gram atomic weight) of "mossy" **zinc was** added to a solution of 81.7 g. (0.5 mole) of trichloro-acetic acid in 400 *cc.* of water and the mixture was stirred mechanically for three hours, when the zinc was completely dissolved and the solution was practically neutral, very slightly acid to litmus, but alkaline to methyl orange and lacmoid. In other experiments 10 g. of zinc in excess of the amount indicated by the equation brought the reaction to an end in one hour and a quarter, and the 10 g. of zinc remained.

The neutral solution resulting from the reaction was diluted to one liter and analyzed for chloride by the Mohr method and for zinc by titration with potassium ferrocyanide: calcd. for the equation given above: Cl, 0.500 gram atomic weight; Zn, 0.500 gram atomic weight. Found: Cl, 0.497; Zn, 0.480.

In another experiment, 53 g. of sodium carbonate (0.5 mole) was added to the neutral solution of zinc salts; the precipitated basic zinc carbonate was filtered off and the solution of sodium salts was evaporated to saturation and transferred to a distilling flask. An excess of concentrated sulfuric acid (75 cc.) was added and the mixture distilled at 25 mm. The fraction which distilled at 105° weighed 24 g. A portion of this distillate was dissolved in benzene and aniline was added. A white crystalline precipitate formed which, after recrystallizing, melted at 123–124°, which is the melting point of aniline dichloro-acetate. The product was further identified by a mixed melting point, using a sample of aniline dichloro-acetate prepared by the method of Doughty and Black.[2] Our acid boiled at 105° and 25 mm. Dichloro-acetic acid is reported[2] to boil at 102" and 20 mm.

In order to obtain some idea as to the energy of the reaction, which is strongly exothermic, 40.8 g. (0.25 mole) of trichloro-acetic acid was dissolved in 400 cc. of water in a thermos bottle which was provided with a one-holed rubber stopper through which passed a thermometer. "Mossy zinc," 16.4 g. (0.25 gram atomic weight) was added and the stopper with the thermometer was put in place. The bottle was shaken frequently and the time and temperatures were as follows.

Minutes	0	10	15	20	30	40	47	80
Temperature, °C	27	42	50	54	57	60	63	67

As in other cases, no hydrogen was evolved, and the solution was neutral (as defined above) at the end of the experiment, and all of the zinc was dissolved. The heat equivalent of the apparatus, as previously determined, was approximately 9.0 calories per degree. The specific heat of the substances present other than water is unknown, but an assumption of 0.25 seems reasonable. From these data we calculate the heat of the reaction as approximately 66,600 calories per mole of trichloro-acetic acid. Of this we can account for approximately 56,600 calories as the heat of formation of 0.5 mole of zinc chloride in solution, leaving approximately 10,000 calories per mole of trichloro-acetic acid for the other items involved in this reaction. No considerable accuracy is claimed for these figures, but they appear to us to have sufficient significance to justify us in mentioning the experiment.

The reaction in benzene is apparently the same as in water, and we have prepared aniline dichloro-acetate by this method also. There does not appear to be any advantage in this method of preparation of dichloro-acetic acid over that described by Doughty and Black.[2]

The corresponding reaction of dichloro-acetic acid with zinc is much less energetic. The amount of heat developed is not impressive, and it was necessary to heat, with stirring, for twelve hours on the water-bath to bring the solution to neutrality and to dissolve the zinc. There was some hydrogen evolved throughout the reaction and when the neutral solution was analyzed only 0.903 gram atomic weight of chlorine was found per mole of dichloro-acetic acid. Evidently in this case 90% of the reaction is similar to that of trichloro-acetic acid with zinc, while the other 10% takes the more usual course as when hydrochloric acid reacts with zinc.

The reaction of monochloro-acetic acid with mossy zinc is very slow, even on the water-bath or at boiling temperature. Time did not permit of a study of this reaction but it was noted that considerable hydrogen was evolved and the solution became neutral after about 100 hours. The analysis was not satisfactory, as apparently some acid was evaporated during the long period of heating. The solution also had some reducing effect on silver salts.

The marked difference in the speed of reaction of the chloro-acetic acids with zinc, and particularly the variation in the type of reaction as well, is interesting in connection with certain observations of one of us[3,4] concerning the reaction of compounds containing a trichloro- or tribromomethyl group with copper and with cuprous chloride in aqueous ammonia solution. It was shown that substances of this class (trihalogen methyl derivatives) are very much more reactive under the given conditions than those having fewer than three halogen atoms joined to one carbon atom.

Conclusion

When trichloro-acetic acid reacts with zinc in water solution, a neutral solution of zinc chloride and zinc dichloro-acetate is obtained. There is no evolution of hydrogen. The reaction is strongly exothermic.

With dichloro-acetic acid the corresponding reaction with zinc is much less exothermic, much slower and hydrogen is evolved to approximately 10% of the amount required by the equation $2HX + Zn = H_2 + ZnX_2$.

With monochloro-acetic acid the reaction is very slow and is to quite a large extent in accordance with the reaction just stated.

The reaction is similar to that in the case of trichloro-acetic acid and copper and an explanation of the mechanism is suggested.

AMHERST, MASSACHUSETTS

---

[3] **Doughty, THIS JOURNAL, 39,2685** (1917).

[4] **Doughty,** *ibid.*, **41,** 1129 (1919).

[Contribution from the Chemical Laboratory of the College of Liberal Arts of Northwestern University]

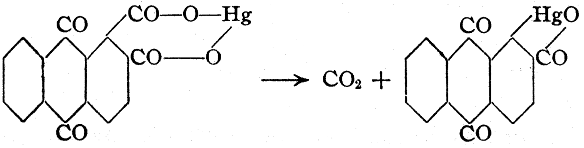
THE MERCURATION OF ANTHRAQUINONEDICARBOXYLIC ACIDS

By Frank C. Whitmore and F. L. Carnahan[1]

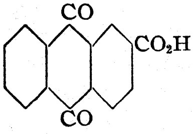
Received October 15, 1928 Published March 6, 1929

The purposes of the present research were to make available mercurated carboxylic acids of relatively high molecular weight and to study further the replacement of one of two ortho carboxyl groups by mercury.[2]

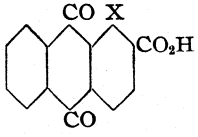
1,2-Anthraquinonedicarboxylic acid was converted to the mercury salt, which was heated dry until no more carbon dioxide was evolved and until ionizable mercury was absent.



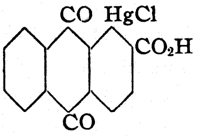
The position of the mercury was proved by treatment with acid, yielding pure anthraquinone-2-carboxylic acid (I) which was shown to be identical with some of the acid prepared by the oxidation of β-methylanthraquinone. Replacement of the mercury by halogen gave the known 1-iodo-anthraquinone-2-carboxylic acid (II) and the hitherto unknown 1-bromo-anthraquinone-2-carboxylic acid (II). The anhydro hydroxymercuri compound was also converted to 1-chloromercuri-anthraquinone-2-carboxylic acid (III).



I



II



III

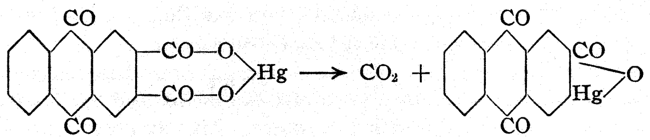
There was no evidence that any of the β-carboxyl was replaced by mercury with the formation of a derivative of anthraquinone-1-carboxylic acid. In other words, the carboxyl replaced was the one between the quinone group and the other carboxyl group.

2,3-Anthraquinonedicarboxylic acid was prepared from the 2,3-dimethyl compound obtained from o-xylene and phthalic anhydride. The mercury salt heated dry decomposed considerably more readily than that of the 1,2-acid.

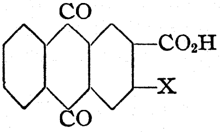
---

[1] Research Fellow in Chemistry, Northwestern University.

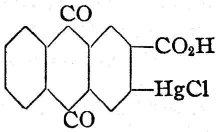
[2] This well-known method of introducing mercury into organic compounds was discovered by Pesci, *Atti accad. Lincei,* [5] **10,** I, 362 (1901).



Treatment of the mercurated product with acid and halogens gave anthraquinone-2-carboxylic acid (I), the known 3-bromo-anthraquinone-2-carboxylic acid (IV) and the new 3-iodo-anthraquinone-2-carboxylic acid (IV). The chloromercuri acid was also prepared (V).



IV



V

Experimental Part

Preparation of **Anthraquinone-1,2-dicarboxylic** Acid.—Naphthalene and phthalic anhydride were condensed in benzene solution in the presence of anhydrous aluminum chloride to form α-naphthoyl-*o*-benzoic acid. Through the elimination of water from this compound by means of concd. sulfuric acid benz-1,2-anthraquinone was obtained. The oxidation of the latter substance with potassium permanganate in strongly acid solution gave anthraquinone-1,2-dicarboxylic acid. Purification of the acid was effected by recrystallization from glacial acetic acid until the melting point was 270°.

Formation of the Mercury Salt of **Anthraquinone-1,2-dicarboxylic** Acid.—To a hot solution of 10 g. of the dibasic acid in 300 cc. of water and 5 g. of potassium hydroxide was added a solution of 7 g. of mercuric oxide in 40 cc. of 50% acetic acid. The resulting mixture contained a slight excess of the dibasic acid and was slightly acid with acetic acid. The mercury salt was immediately precipitated as a slightly yellow powder upon mixing the two solutions. It was filtered off, thoroughly washed with hot water, dried and pulverized. The yield was about 95%.

Establishment of a Carbon–Mercury Linkage in **Anthraquinone-1,2-dicarboxylic** Acid.—Refluxing of suspensions of the mercury salt in dilute acetic acid solution did not split out carbon dioxide to form a carbon–mercury linkage. Attempts were made under a wide range of conditions. To effect the desired result, it was found necessary to heat the dry mercury salt at 235°. No evolution of carbon dioxide was perceptible at lower temperatures.

The pulverized mercury salt was placed in a small flask which was immersed in a fused salt bath (potassium nitrate and sodium nitrite) held at 235°. A convenient amount of the mercury salt for a 200-cc. flask was 15 g. The material was frequently stirred in order to insure a uniform product. Small amounts of the material were tested from time to time for the presence of inorganic mercury by suspending in dilute acetic acid and adding a bright piece of copper wire. An amalgamation of the surface of the copper on heating the above mixture to boiling was taken to indicate the presence of inorganic mercury. This test was the most reliable one available. A minimum of eight hours' heating at 235° was required to obtain a product giving no test for inorganic mercury. The material thus obtained was almost entirely alkali-soluble, though long boiling with alkali was necessary to effect solution. Longer heating of the mercury salt gave a larger amount of alkali-insoluble material. The mercuration product as obtained in this way was a bright yellow powder. It did not melt and decomposed only on heating above 300°.

A suspension of 2 g. of the finely pulverized mercuration product in 400 cc. of water was boiled for five minutes with 25 cc. of concd. hydrochloric acid. The undissolved material was filtered and washed with hot water. It was then boiled with a dilute solution of ammonia for one minute. The material unchanged by this treatment was filtered and thoroughly washed with hot water. This treatment should suffice to eliminate both acidic and basic impurities. The material was then dried and analyzed.

Anal. Subs., 0.2517, 0.2310: Hg, 0.1128, 0.1030. Calcd. for $C_{15}H_6O_4Hg$: Hg, 44.5. Found: Hg, 44.8, 44.6.

Treatment of the Mercuration Product with Hydrochloric Acid.—A mixture of 10 g. of the mercuration product and 500 cc. of concd. hydrochloric acid was boiled for twenty-four hours. The reaction mixture was diluted with twice its volume of water and filtered. The residue was washed with warm water and extracted with dilute sodium hydroxide.

The alkali-insoluble material did not change on further boiling with concd. hydrochloric acid. It contained no mercury. On boiling with *aqua regia* anthraquinone was formed. The presence of this alkali-insoluble material was perhaps due to the action of hydrochloric acid on the monobasic anthraquinone acid. The 2-acid on boiling with concd. hydrochloric acid forms an alkali-insoluble product. Anthraquinone itself even on long boiling with concd. hydrochloric acid is unchanged.

The alkali-soluble material was precipitated from solution by the addition of hydrochloric acid. This material on drying weighed 4.25 g. (76.6% yield). It melted at 281–282° without further purification. The melting point after two crystallizations from glacial acetic acid was 285–285.5°. Investigation of the various fractions from the acetic acid crystallizations failed to show the presence of any other product.

Preparation of Anthraquinone-2-carboxylic Acid.—A solution of 40 g. of β-methylanthraquinone in 800 cc. of concd. sulfuric acid was added to 1600 cc. of hot water in a 3-gallon crock with vigorous mechanical stirring. To the suspension of β-methylanthraquinone thus produced was gradually added 60 g. of finely-powdered potassium permanganate. The reaction was allowed to continue with vigorous mechanical stirring for ten minutes after the addition of all of the permanganate. The mixture was then decolorized by the addition of a hot solution of oxalic acid. The insoluble material was collected on a filter and extracted with hot dilute ammonia solution. The insoluble residue from this treatment was unchanged β-methylanthraquinone. The ammoniacal solution was acidified with hydrochloric acid and the precipitated material filtered off. The crude acid was treated with decolorizing carbon in boiling glacial acetic acid. The solution was filtered and allowed to crystallize. The first crop of crystals melted at 285–286°. The melting point was unchanged by further recrystallization from glacial acetic acid. A mixed melting point of this acid with that obtained by the action of hydrochloric acid on the mercuration product was 285–286°, an indication of the identity of the two materials.

Formation of I-Iodo-anthraquinone-2-carboxylic acid.—The position of the mercury in the anhydro compound was further established by the formation of this acid on replacing mercury by iodine. A mixture of 6.75 g. (0.015 mole) of the mercurated product, 7.47 g. (0.045 mole) of potassium iodide and 3 81 g. (0.015 mole) of iodine and 200 cc. of water was heated at 70° for about three hours, or until the iodine was entirely used up. The presence of about 3 cc. of chloroform was found to be very helpful in the estimation of the amount of iodine present at any time. When the iodine had all reacted, the mixture was filtered while hot. The filtrate was acidified with hydrochloric acid and the deep yellow precipitate was collected on a filter. This was washed with a little potassium iodide solution and then with warm water. On crystallization from 95% ethyl alcohol the substance was obtained in very fine, deep yellow needle crystals which became orange colored on standing; melting point 266–268°. The melting point given in the literature is 266–267°.

Anal. Subs., 0.2518, 0.2606: 0.100 *N* $AgNO_3$, 6.72 cc., 6.94 cc. Calcd. for $C_{15}H_7O_4I$: I, 33.6; Found: I, 33.9, 33.8.

Preparation of 1-Bromo-anthraquinone-2-carboxylic Acid.—This previously undescribed acid was obtained in a fashion analogous to that used for the iodo acid. A suspension of 5 g. of the mercurated product in 500 cc of water was heated at 50° for three hours with an excess of bromine in sodium bromide solution At the end of this time the excess bromine was boiled off. The mixture was filtered while hot. The filtrate on acidification with hydrochloric acid gave a slightly yellow flocculent precipitate. This was filtered off, washed with warm water and dried, yield, 1.37 g. Apparently only a part of the mercury had been replaced, since 2.15 g. of the original material was recovered apparently unchanged. Crystallization from alcohol gave yellow needles, melting at 267–268°. As in the case of the corresponding iodo acid the needles were extremely fine.

Anal. Subs., 0.1589: 0.100 N $AgNO_3$, 4.80 cc. Calcd. for $C_{15}H_7O_4Br$: Br, 24.1. Found: Br, 24.2.

Preparation of 1-Chloromercuri-anthraquinone-2-carboxylic Acid.—A mixture of 5 g. of the mercurated product, 20 g. of sodium hydroxide and 500 cc. of water was heated just below boiling for twelve hours. The mixture was filtered hot and made barely acid with hydrochloric acid at the boiling point of the solution. After standing for a few minutes, it was made alkaline with 2 N sodium hydroxide solution and then just acid with hydrochloric acid. These operations were all carried out at the boiling point; otherwise filtration was very difficult and the precipitate likely to be very impure. The precipitated material was filtered off, washed thoroughly with hot water, dried and pulverized. The compound as thus obtained was a light yellow powder.

Anal. Subs., 0.2017, 0 2006: Hg, 0.0824, 0.0820. Subs, 0.1978, 0.2032: 4.00, 4.18 cc. of 0.100 N $AgNO_3$. Calcd. for $C_{15}H_7O_4ClHg$: Hg, 41.2; Cl, 7.28. Found: Hg, 40.9, 40.9; Cl, 7.16, 7.37.

Preparation of Anthraquinone-2,3-dicarboxylic Acid.—*o*-Xylene was condensed with phthalic anhydride in the presence of anhydrous aluminum chloride, high boiling naphtha being used as a diluent. The o-xyloyl-o-benzoic acid thus formed gave 2,3-dimethylanthraquinone on dehydration with 15–20% fuming sulfuric acid. Dimethylanthraquinone was oxidized to the dibasic acid as follows.

A solution of 40 g of 2.3-dimethylanthraquinone in 800 g. of concd sulfuric acid was added with vigorous mechanical stirring to 1600 g. of hot water in a 3-gallon crock. To the suspension of dimethylanthraquinone thus obtained was added in small portions 120 g. of finely-powdered potassium permanganate The addition was made at such a rate as to maintain the temperature at 90–95°. The reaction was allowed to continue for ten minutes with mechanical stirring after the addition of all the permanganate. The excess oxidizing agent was then removed by oxalic acid. The insoluble material was filtered off and washed with hot water It was transferred to a beaker and the acid dissolved in hot dilute ammonia solution. The residue of unchanged dimethylanthraquinone was removed by filtration. The dibasic acid was precipitated from the filtrate by the addition of hydrochloric acid. The material was filtered, thoroughly washed with hot water and dried; yield, 7.5 g. The amount of recovered dimethylanthraquinone was 21 g. The yield of the acid was 31.6%, based on the material which reacted. Purification was effected by crystallization from glacial acetic acid. The melting point of the material thus obtained was 340–342°.

Preparation of the Mercury Salt of Anthraquinone-2,3-dicarboxylic Acid.—To a hot solution of 7.5 g. of the acid in 500 cc. of water and 50 cc. of 2 N potassium hydroxide was added a solution of 5.25 g. of mercuric oxide in 30 cc. of 50% acetic acid. The mercury salt was immediately precipitated as a slightly yellow powder. The above procedure provided for a slight excess of the dibasic acid and the resulting mixture was slightly acid with acetic acid. The material was filtered off, washed with a large quantity of hot water, dried and pulverized. The yield was about 95%.

Establishment of a Carbon–Mercury Linkage in Anthraquinone-2,3-dicarboxylic Acid.—In a 200-cc. flask was placed 11 g. of the finely-powdered mercury salt of anthraquinone-2,3-dicarboxylic acid. The flask was heated in a fused salt-bath. The evolution of carbon dioxide was tested for from time to time as the temperature was raised. At 210–215" the evolution of carbon dioxide was first noticed. At this temperature the gas came off quite rapidly. The contents of the flask were stirred from time to time to insure uniform treatment of the material. At the end of four or five hours, no test could be obtained for inorganic mercury by the previously described copper wire method. The product was a bright yellow powder. Sublimed yellow needles and free mercury were evidence that some decomposition took place under the conditions used. The amount of material recovered was 8.72 g.

The mercurated product required purification before analysis, since it was not at all homogeneous. The possible impurities such as the original acid, anthraquinone and mercuric oxide are soluble in glacial acetic acid. Accordingly, 2 g. of the mercurated product was boiled for five minutes with 50 cc. of glacial acetic acid. The material undissolved by this treatment was filtered, dried and analyzed.

Anal. Subs., 0.2308, 0.2333: Hg, 0.1015, 0.1027. Calcd. for $C_{15}H_6O_4Hg$: Hg, 44.5. Found: Hg, 44.0, 44 0.

As in the case of the 1,2-dibasic acid, the formation of a mercuri-*bis* acid or a double mercuri-*bis* compound might be possible. No evidence was obtained for the formation of such products. The mercurated product after the above treatment was almost entirely soluble in alkali, though solution was very slow. The formation of two isomeric anhydro-*o*-hydroxymercuri acids was not possible here as in the case of the 1,2-dibasic acid.

Treatment of the Mercuration Product with Hydrochloric Acid.—A mixture of 3.00 g. of the mercurated product and 150 cc. of concd. hydrochloric acid was refluxed for fifteen hours. The reaction mixture was diluted with twice its volume of water, allowed to stand for a short time and filtered. The insoluble material was extracted with dilute ammonium hydroxide. The extract was acidified with hydrochloric acid. A slightly yellow flocculent substance was precipitated. The mixture was allowed to digest on the steam-bath for about an hour. The precipitated material was filtered off, washed with warm water and dried; yield, 1.49 g. The various filtrates were collected and evaporated to dryness together.

The material insoluble in ammonia was boiled with glacial acetic acid. Its original weight was 0.12 g. The amount soluble in acetic acid was 0.06 g. This was probably a substance formed by the action of hydrochloric acid on the anthraquinone acid. The insoluble material was probably unchanged mercury compound.

The material soluble in ammonia solution was the main product. It was dissolved in boiling glacial acetic acid and treated with decolorizing carbon and filtered. The filtrate on cooling deposited small felted crystals of a slightly yellow color; melting point, 280–281°. Further crystallization from the same solvent raised the melting point to 284–285°. A mixture with the 2-acid from the oxidation of β-methylanthraquinone melted at 284.5–285.5°.

The residue from the evaporation of the various filtrates was taken up in 25 cc. of water slightly acidulated with hydrochloric acid. The insoluble portion was collected on a filter. It weighed 0.10 g. It did not melt and seemed to consist largely of inorganic material.

The amount of the mercury compound reacting was 3.00 g. − 0.06 g. = 2.94 g. Assuming that the material insoluble in alkali but soluble in acetic acid is formed from an approximately equal weight of the 2-acid of anthraquinone, the amount of material accounted for is 1.49 g. + 0.06 g. = 1.55 g. The amount of the monobasic anthraquinone acid which would be formed from 2.94 g. of the anhydro compound is 1.65 g. The amount of material accounted for is thus about 94%.

Preparation of 3-Bromo-anthraquinone-2-carboxylic Acid.—A suspension of 2 g. of the mercury compound in 200 cc. of water was treated with an excess of bromine in potassium bromide. The mixture was heated at 50–60° for two hours under reflux to prevent the loss of bromine. The excess of bromine was then boiled off under a hood. The mixture was filtered and the filtrate acidified with hydrochloric acid. The mixture was allowed to digest on the steam-bath for about an hour. The product, after washing with warm water and drying, weighed 0.95 g. (yield 65%). After two crystallizations from 70% alcohol, it was obtained in very fine, almost colorless felted needles. These melted at 284–285.5°. The value given in the literature is 284°.

Anal. Subs, 0.1556: 0 100 *N* $AgNO_3$, 4.62 cc. Calcd. for $C_{15}H_7O_4Br$: Br, 24.1. Pound: Br, 23.7.

Preparation of 3-Iodo-anthraquinone-2-carboxylic Acid.—The previously undescribed iodo acid was prepared in a fashion analogous to that for the corresponding bromine compound. To a solution of 1.27 g. of iodine and 2.50 g. of potassium iodide in 200 cc. of water was added 2.25 g. (0.05 mole) of the mercury compound. The mixture was heated at 60° under a condenser until the iodine had all reacted (three to four hours). The insoluble material, usually small in amount, was removed by filtration. The filtrate was acidified with hydrochloric acid. The precipitated material was filtered after digestion on the steam-bath for about an hour, washed with a little potassium iodide solution to insure the removal of mercuric iodide, then with water at about 60° and dried. The crude yield was 1.37 g. or 72.5%.

On crystallization from alcohol the substance was obtained in extremely fine felted crystals of a bright yellow color. These melted at 289–290°.

Anal. Subs., 0.2042: 0.100 *N* $AgNO_3$, 5 36 cc. Calcd. for $C_{15}H_7O_4I$: I, 33.6. Found: I, 33.3.

Preparation of 3-Chloromercuri-anthraquinone-2-carboxylc Acid.—A mixture of 2 g. of the mercury compound, 50 cc. of 2 *N* sodium hydroxide and 450 cc. of water was refluxed for twelve hours. Any residue was filtered off. The filtrate was heated to boiling and made strongly acid with hydrochloric acid. A flocculent yellow precipitate was formed. After standing for three minutes the mixture was neutralized with 2 N sodium hydroxide. It was then made slightly acid with hydrochloric acid to precipitate the chloromercuri acid, the procedure again being carried out at the boiling point. The precipitation had to be made at the boiling point; otherwise the material precipitated was very difficult to filter and to wash free of the impurities which it contained. The product was filtered off and thoroughly washed with hot water. After drying it was pulverized and boiled for five minutes with 25 cc. of glacial acetic acid. It was washed and dried. The chloromercuri acid is a light yellow powder. Its alkaline solution is a deep red color.

Anal. Subs., 0.1996, 0.2488: Hg,[3] 0.0818, 0.1015. Subs., 0.2500: 5.32 cc. of

---

[3] In the usual gold crucible analysis an unusually high temperature was required for decomposition of this compound.

0.100 N $AgNO_3$. Calcd. for $C_{15}H_7O_4ClHg$: Hg, 41.2; Cl, 7.28. Found: Hg, 40.9, 40.8; Cl, 7.54.

All melting point temperatures given in this paper are uncorrected. The correction for temperatures used is about 4°.

All mercury analyses were made by the gold crucible method.[4]

In halogen analyses the materials were decomposed by the use of sodium peroxide as outlined in Kingscott and Knight, "Organic Analysis." The amount of halogen was then determined by the Volhard method.

Summary

1. The mercury salts of the 1,2- and the 2,3-dicarboxylic acids of anthraquinone lose carbon dioxide when heated above 200°. In each case a mercury–carbon linkage is established. In the 1,2-acid the replacement is limited to the carboxyl between the quinone group and the other carboxyl, that is, only the a-carboxyl is replaced.
2. The mercury salt of the 2,3-acid loses carbon dioxide more readily than that of the 1,2-acid.
3. The corresponding chloromercuri compounds have been prepared.
4. The mercury has been replaced by bromine and by iodine.
5. The following new compounds have been prepared: anhydro-1-hydroxymercuri-anthraquinone-2-carboxylic acid, 1-chloromercuri-anthraquinone-2-carboxylic acid, 1-bromo-anthraquinone-2-carboxylic acid, anhydro-3-hydroxymercuri-anthraquinone-2-carboxylic acid, 3-chloromercuri-anthraquinone-2-carboxylic acid, 3-iodo-anthraquinone-2-carboxylic acid.
6. A new method has been developed for preparing anthraquinone-2,3-dicarboxylic acid.

EVANSTON, ILLINOIS

---

[4] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Inc., New York, 1922, p. 365.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE BROMINATION OF PYRIDINE[1]

BY S. MARY ELIZABETH ENGLERT AND S. M. MCELVAIN

RECEIVED OCTOBER 22,1928 PUBLISHED MARCH 6, 1929

The preparation of 3-bromopyridine and 3,5-dibromopyridine by the direct bromination of pyridine has long been known as a rather difficult reaction to carry out. Nevertheless, it appears to be the simplest method available for the preparation of these particular bromopyridines in quantity. Hofmann[2] was able to prepare 3,5-dibromopyridine by heating pyridine dibromide, $C_5H_5N\cdot Br_2$, in a sealed tube for one hour at 200°. He obtained the same product by heating pyridine hydrochloride and bromine together in a sealed tube. In neither reaction did he report the formation of 3-bromopyridine. Later, Ciamician and Silber[3] prepared 3-bromopyridine along with 3,5-dibromopyridine by heating pyridine hydrochloride and bromine in a sealed tube as Hofmann had done. They, however, heated their mixture for a longer time (twenty-four hours) and at a higher temperature (210–230°). Their combined yield of the mono- and dibromopyridines was only 21% of the theoretical. Blau[4] reported an improvement over the earlier sealed-tube methods, which consisted essentially of passing a mixture of bromine and carbon dioxide through molten pyridine hydrochloride. By this procedure the combined yield of the mono- and dibromopyridines was 42% of the theoretical.

This communication reports what seems to be a distinct improvement over all of the older methods of bromination of pyridine. The procedure consists of heating a perbromide of pyridine hydrobromide at 230–250° under ordinary pressure until the evolution of hydrogen bromide ceases.

There appears to be considerable variation in the composition of the perbromides of pyridine and pyridine salts as reported in the literature. Anderson[6] and Hofmann[2] treated pyridine and pyridine hydrochloride in aqueous solution with bromine and obtained crystalline precipitates which showed fair stability and to which they assigned the formula $C_5H_5N\cdot Br_2$. Grimaux[6] treated pure pyridine with bromine and obtained a compound that crystallized in thin, red plates and melted at 126°. To this compound he assigned the formula $(C_5H_5N\cdot Br_2)_2\cdot HBr$. Trowbridge and

---

[1] A portion of the thesis submitted by S. Mary Elizabeth Englert to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science.

[2] Hofmann, Ber., 12, 988 (1879).

[3] Ciamician and Silber, *Ber.*, 18,722 (1885).

[4] Blau, *Monatsh.,* 10, 372 (1889).

[5] Anderson, *Ann.*, 105, 341 (1858).

[6] Grimaux, *Compt. rend.,* 95, 85 (1882).

Diehl[7] were unable to obtain a definite compound from bromine and pyridine in aqueous solution but in chloroform solution they obtained a compound which appeared to have the formula $C_5H_5N{\cdot}Br_4$. On standing this tetrabromide lost bromine and passed into a compound which analysis showed to have the formula $C_5H_5N{\cdot}Br_2$. Barthe[8] obtained from pyridine and bromine a perbromide to which he assigned the formula $C_5H_5N{\cdot}Br$. Trowbridge and Diehl also prepared perbromides of salts of pyridine. By passing bromine into an aqueous solution of pyridine hydrobromide they obtained two perbromides, one of which contained 41.95% of bromine and the other 33.66% of bromine that was present as perbromide bromine. The latter compound melted at 93° and the formula $C_5H_5N{\cdot}HBr{\cdot}Br$ was assigned to it. The perbromide containing 41.95% of perbromide bromine was assumed to be a mixture of $C_5H_5N{\cdot}HBr{\cdot}Br_2$ and $C_5H_5N{\cdot}HBr{\cdot}Br$. These investigators also prepared a perbromide in aqueous solution to which they assigned the formula $C_5H_5N{\cdot}HBr{\cdot}Br_2{\cdot}H_2O$. It melted at 118–120° and contained 67.96% of perbromide bromine.

In the work which is reported here it was found that glacial acetic acid was a much better solvent than water for the preparation of these perbromides because both reactants (bromine and pyridine hydrobromide) were quite soluble in this medium and the perbromides which were formed, while very soluble in warm acetic acid, were quite insoluble in the cold acid. From one mole of bromine and one mole of pyridine hydrobromide in acetic acid solution there was obtained a perbromide that melted at 132–134". The yield was 95–97% of the theoretical based on the formation of $C_5H_5N{\cdot}HBr{\cdot}Br_2$. While this formula requires 50% perbromide bromine content, there was found only 47% of perbromide bromine in the product that melted at 132–134°.

One mole of pyridine hydrobromide and one-half mole of bromine in glacial acetic acid solution gave a perbromide that melted at 101–103° and had 39.7% of perbromide bromine. The perbromide bromine in the compound of the formula $C_5H_5N{\cdot}HBr{\cdot}Br$ amounts to 33.3%. The authors are not able as yet to assign satisfactory formulas to these perbromides but it is hoped that further work will throw some light on this subject.

An attempt was made to use pyridine hydrochloride instead of pyridine hydrobromide for the preparation of these perbromides but it was found that the yields from the hydrochloride were considerably lower than those from the hydrobromide and that the perbromides of pyridine hydrochloride were very deliquescent and quite difficult to handle.

When these perbromides were heated at 230–250" under a reflux condenser, there was a vigorous evolution of hydrogen bromide with the formation of 3-bromo- and 3,5-dibromopyridine. The perbromide containing 47%

---

[7] Trowbridge and Diehl, THIS JOURNAL, 19,558 (1897).

[8] Barthe, *Compt.* rend., 145, 75 (1907).

of perbromide bromine gave a 40% yield of 3,5-dibromopyridine but none of the 3-bromopyridine. A mixture of pyridine hydrobromide and this perbromide gave a 35% yield of 3-bromopyridine and a 10% yield of the dibromopyridine. 'She greatest yields of brominated pyridines were obtained when the lower perbromide was heated. In this case 36–38% yields of 3-bromopyridine and 30–36% yields of 3,5-dibromopyridine were obtained. The yield calculations were made on the basis of the bromine used in the preparation of the perbromides.

Experimental

Pyridine Hydrobromide Perbromide (47% Perbromide Bromine).—To a warm (60–65°) solution of 160 g. (1 mole) of pyridine hydrobromide in 240 g. of glacial acetic acid in a large beaker, a solution of 160 g. (1 mole) of bromine in 160 g. of acetic acid was added. The resulting solution was stirred thoroughly by hand and then allowed to cool. After two to three hours there was deposited a mass of large, orange-red, needle-shaped crystals. They were filtered off and dried in a desiccator. They were quite stable and when dry melted at 132–134°. The yield was 300–310 g. (95–97% based on the formation of $C_5H_5N \cdot HBr \cdot Br_2$). These crystals were analyzed for perbromide bromine by the method of Trowbridge and Diehl[7] and found to contain 47.0% of such bromine.

Pyridine Hydrobromide Perbromide (39.7% Perbromide Bromine).——This perbromide was prepared in exactly the same manner as the one described above except that 80 g. (0.5 mole) of bromine in 80 g. of acetic acid was added to the warm solution of 160 g. of pyridine hydrobromide in acetic acid. The crystals obtained melted at 101–103° and the yield averaged 205 g. Analysis showed 39.7% of perbromide bromine. There was no appreciable change in weight in either of these perbromides when they were allowed to stand in a vacuum desiccator over sulfuric acid for several days.

3-Bromopyridine and **3,5-Dibromopyridine.**—These products were prepared in better yields from the lower perbromide. The perbromide containing 39.7% of bromine as perbromide as obtained in the preparation described above was mixed with the residue left by the evaporation of the acetic acid mother liquors. The weight of this mixture amounted to approximately the sum of the weights of pyridine hydrobromide and bromine (that is, 240 g.) used in the preparation of the perbromide. This solid mixture was heated in a round-bottomed flask under a reflux condenser in a sodium nitrate–potassium nitrate bath that was maintained at 230–250°. The solid melted at about 100° and as the liquid reached the bath temperature there was a vigorous evolution of hydrogen bromide. The evolution of hydrogen bromide gradually subsided and at the end of six to eight hours had practically ceased. During the reaction there was considerable condensation of crystals of 3,5-dibromopyridine on the cooler parts of the flask and in the reflux condenser. When the evolution of hydrogen bromide had ceased, the reaction mixture was steam distilled until no more crystals of 3,5-dibromopyridine appeared in the condenser. The distillate consisted of an acid solution and suspension of 3,5-dibromopyridine which was completely precipitated out by the addition of alkali. The precipitate was filtered off and recrystallized from alcohol. The yield was 18–22 g. of a product that melted at 110–111°. The residue left in the flask after the removal of the 3,5-dibromopyridine by steam distillation was made strongly alkaline with sodium hydroxide and again steam distilled. The distillate consisted of water, pyridine and 3-bromopyridine and as it first came over was clear, but as the proportion of water increased it became turbid and when about 250 cc. of distillate had been collected, a layer of 3-bromopyridine and some pyridine was present in the receiver. This layer was separated, dried with solid sodium hydroxide and fractionated. The fraction that boiled at 160–175° amounted to 29–31 g. On redistillation practically all of this fraction boiled at 168–172°. The yield of the dibromopyridine was 30–36% of the theoretical and that of the 3-bromopyridine 36–38% of the theoretical based on the bromine used in the preparation of the perbromide.

The separation of 3,5-dibromopyridine from 3-bromopyridine by steam distillation of the former from acid solution was originally used by Ciamician and Silber[3] and is fairly satisfactory but not complete. There appears to be some of the di-substitution product left with the monobromopyridine even after prolonged steam distillation, and in the final distillation of the latter compound a small amount of the dibromopyridine usually crystallizes in the condenser.

When the perbromide of higher bromine content was heated under similar conditions, a 40% yield of the dibromopyridine was obtained but none of the 3-bromopyridine was found. It was thought that dilution of this higher perbromide with pyridine hydrobromide might increase the yield of the mono-substituted product but several runs in which 2 moles of pyridine hydrobromide was mixed with 1 mole of the higher perbromide gave an average of 10% yield of 3-bromopyridine and 30% yield of the 3,5-dibromopyridine.

Summary

A convenient method of brominating pyridine to 3-bromopyridine and 3,5-dibromopyridine has been described. It consists of the preparation of a perbromide of pyridine hydrobromide in glacial acetic acid solution and the transformation of this perbromide by heat into the bromopyridines.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

SYNTHETIC GLYCERIDES. I. PREPARATION AND MELTING POINTS OF GLYCERIDES OF KNOWN CONSTITUTION[1]

BY H. P. AVERILL, J. N. ROCHE AND C. G. KING

RECEIVED OCTOBER 22, 1928 PUBLISHED MARCH 6, 1929

The isolation of pure triglycerides from natural fats and oils is an uncertain and laborious process because of the difficulty of complete separation. Even when pure triglycerides have apparently been obtained satisfactory evidence is not available to indicate which of the possible isomers has been found. It was thought that progress could best be made through the synthesis of glycerides of known constitution and the study of their chemical and physical properties. Data thus obtained will be valuable in the study of the components of naturally occurring fats and oils.

It seemed probable that definite relationships might be found between certain physical properties of the fats and their molecular structure if sufficient data were available to warrant conclusions. The three sets of isomers (only one having fatty acids) prepared by Fischer[2] indicated that

---

[1] This paper is based upon a part of the theses submitted by H. P. Averill and J. N. Roche to the Graduate School, University of Pittsburgh, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] E. Fischer, *Ber.*, 53, 1621 (1920).

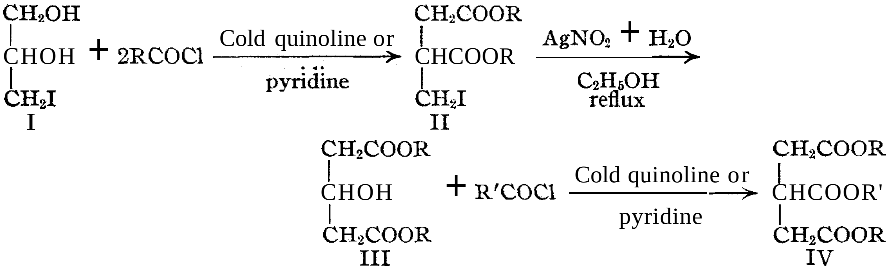
the unsymmetrical glycerides melt at a lower temperature than their symmetrical isomers and may differ somewhat in solubility, but much of the data in the literature is in conflict with this generalization.

A review of the literature on the synthesis of fats shows that there are seven general methods for preparing simple and mixed glycerides[3] Only two or possibly three of these methods, however, are found to be of value in the preparation of glycerides in which the position of the acyl groups can be stated with certainty. Four of the general methods are due to Griin and his co-workers and much of the data on synthetic glycerides found in the literature is based on these reactions. Three of Grüns' methods have been found to result in an unpredictable rearrangement of the acyl groups. It is found-that the replacement of an OH group in glycerol at elevated temperatures by an acyl chloride or the replacement of a halogen by an OH group-will always allow of a shifting of the acyl groups already present into their most natural positions. Not only is the separation of the individual components of such mixtures difficult to perform but they are further complicated because at the temperatures employed there can be reactions between two moles of the partly acylated glycerides.

The preparation of glycerides from halohydrins and soaps, a fourth method used extensively by Griin, while allowing of greater freedom from shifting, permits of side reactions of considerable magnitude.

Fischer, shortly before his death in 1920, devised an entirely new method for the preparation of unsymmetrical triglycerides and greatly improved the synthesis of symmetrical di- and triglycerides and by these methods glycerides can now be prepared whose chemical structure is reasonably certain.

The synthesis of symmetrical mixed glycerides by the Fischer method can best be shown by the following reactions



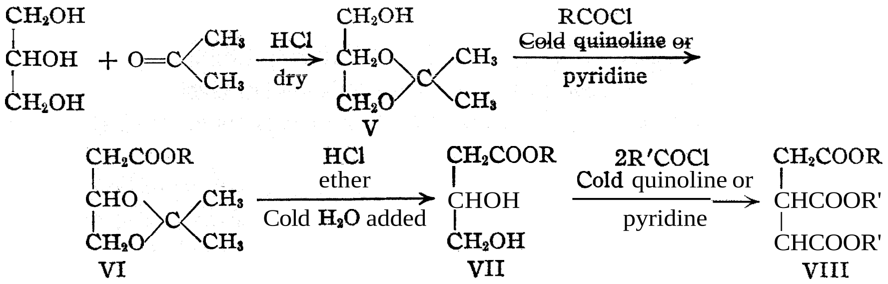
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2I \\ \quad I \end{array} + 2RCOCl \xrightarrow[\text{pyridine}]{\text{Cold quinoline or}} \begin{array}{l} CH_2COOR \\ | \\ CHCOOR \\ | \\ CH_2I \\ \quad II \end{array} \xrightarrow[\substack{C_2H_5OH \\ \text{reflux}}]{AgNO_2 + H_2O}$$

$$\begin{array}{l} CH_2COOR \\ | \\ CHOH \\ | \\ CH_2COOR \\ \quad III \end{array} + R'COCl \xrightarrow[\text{pyridine}]{\text{Cold quinoline or}} \begin{array}{l} CH_2COOR \\ | \\ CHCOOR' \\ | \\ CH_2COOR \\ \quad IV \end{array}$$

The synthesis of unsymmetrical mixed triglycerides can be shown by the following reactions

---

[3] A. Griin and E. Theimer, *Ber.*, **40**, 1792 (1907); A. Griin and P. Schacht, *ibid.*, 40,1778 (1908); A. Griin and F. Wittka, *ibid.*, **54B**, 273,290 (1921); A. Fairbourne and G. E. Foster, *J. Chem. Soc.*, *127*, 2760 (1925); E. Abderhalden and E. Eichwald, *Ber.*, **48**, 1849 (1915); E. Fischer, M. Bergwin and H. Barwind, *ibid.*, [2] 53, 1589 (1920); C. Amberger and K. Bromig, *Biochem. Z.*, 130,252 (1922).



No temperatures higher than 30–35° need be employed in these syntheses except for the conversion of the diacylated iodohydrin wherein the alcohol mixture is refluxed and the acyl group shifts from the β- to the a-position following hydrolysis of the halide. All intermediate compounds can be purified by crystallization or vacuum distillation before use in the next step.

Thus it is only within the last few years that a study of the physical properties of the isomeric glycerides has been possible. In view of the uncertainty of the data for many of the mono-, di- and triglycerides reported in the literature, this investigation was undertaken (a) to recheck many of the values given in the literature, (b) to synthesize other glycerides by methods which have been found satisfactory and (c) to find what relation exists between the constitution of the isomeric glycerides and their physical properties. Data are included in this paper only with respect to their melting points. Further data will be given in later papers.

Preparation of Acyl Chlorides.—Acyl chlorides were prepared by the use of oxalyl chloride and fatty acid according to the directions given by Adams and Ulich.[4] The following acyl chlorides were prepared: n-capryl, b. p. 104–105 (9 mm.); myristyl, b. p. 134° (2.5 mm.); stearyl, b. p. 165° (0.4 mm.); lauryl, b. p. 150° (22 mm.); caproyl, b. p. 138–140° (atmos.).

Stearyl chloride could only be distilled when the distilling flask was immersed up to the side arm in a special oil-bath. The top of the bath was heated by means of a hot-plate and the temperature maintained throughout the bath at 167'. All compounds of this type were kept in desiccators over phosphorus pentoxide.

Preparation of **α-Monoglycerides.**—The preparation of a-monomyristin will show the general procedure used in the preparation of monoglycerides.

To a mixture of 8.82 g. (1.1 moles) of acetoneglycerin and 8.85 g. (1.1 moles) of quinoline (pyridine used for low mol. wt. fatty acids) contained in a thin, glass-stoppered iodine flask, there was added, with cooling in an ice-bath, 15 g. (1 mole) of myristyl chloride. After standing at room temperature for two days, it was treated with 100 cc. of ether and 60 cc. of ice-cold, 0.5 N sulfuric acid. The mixture was shaken in a separatory funnel and the acid layer drawn off. After several washings with the ice-cold acid, no test for quinoline was found and the ether layer was then thoroughly

---

[4] R. Adams and L. Ulich, THIS JOURNAL, 42, 599 (1920).

shaken several times with 75-cc. portions of potassium bicarbonate and finally washed well with water. After drying over fused sodium sulfate, the ether was evaporated and the myristylacetoneglycerin purified.

The hydrolysis of the acetone compound was carried out by two different methods. (a) To the acetone compound obtained above dissolved in 75 cc. of th[illegible] 80 c[illegible] of concentrated hydrochloric acid was slowly added. The mixture was kept in a cold water-bath for half an hour and then treated with 300 cc. of water. The mixture was next placed in a freezing mixture and the monomyristin soon separated in the form of fine white crystals. After suction-filtering and washing with water, the crystals were dried over phosphorus pentoxide and crystallized from a 1:1 mixture of ether and petroleum ether. Lustrous plates or leaves separated which melted at 67.3'; the melting point did not change on repeated recrystallization.

(b) Ten grams of the myristylacetoneglycerin was shaken with 40 cc. of 0.25 *N* sulfuric acid at 45°. The mixture was left in a 40'-oven for twenty-four hours. It was then cooled to 0° and treated with a slight excess of barium hydroxide. The excess hydroxide was removed by carbon dioxide and the mixture evaporated without filtration at 40°. The residue was treated with chloroform and the chloroform solution filtered from the carbonate and sulfate and dried over fused sodium sulfate. After evaporation of the chloroform the monomyristin was crystallized from 1:1 ether and petroleum ether; melting point 67.2'.

The following a-monoglycerides were prepared according to the above method.

Compound	M. p., °C., found	Previously recorded
a-Monopalmitin	77.0	78–79 (a), 77.6 (d), 63 (h), 72 (g), 65 (e), 58 (i)
a-Monomyristin	67.3	68 (g), 68 (j)
α-Monocaprin	51.4	
a-Monolaurin	63.0	62-63 (a), 52 (b), 61 (c), 59 (b), 58 (c)
a-Monostearin	81.1	81–82 (a), 80.9 (d), 73 (e), 61 (f), 78 (g)
a-Monoacetin	Not distilled	

(a) *Ber.*, 53, 1589 (1920); (b) *ibid.*, 42, 3750 (1909); (c) *ibid.*, 43, 1283 (1910); (d) *Biochem.* Z., 130, 252 (1922); (e) Z. *Biol.*, 44, 78 (1903); (f) *Chim. Org.* Syn., II, 65 (1860); (g) *Ber.*, 36, 4339 (1903); (h) Ann., 6, 225 (1884); (i) *Chim. Org. Syn.*, II, 75 (1860); (j) *Ber.*, 45, 3420 (1912).

Preparation of α,α-Diglycerides.—α,α-Diglycerides were prepared according to the following method, showing the preparation of a, a-dilaurin.

Ten and one-tenth g. (1 mole) of a-iodohydrin in 13.8 cc. (1 mole) of quinoline was cooled to 0° in ice water. To the mixture, which was kept cold, 22.0 g. (1 mole) of lauryl chloride in 42 cc. of chloroform was added in several portions. After standing at room temperature for forty-eight hours the red-colored reaction mixture was taken up with 400 cc. of ether and 100 cc. of ice-cold 0.5 N sulfuric acid. The washing with acid, bicarbonate and water was carried on in the same manner as for monoglycerides. After drying the solution the ether was evaporated and the a-iodo-dilaurin remained as a colorless oil. By dissolving in a mixture of ether and methyl alcohol (1:3) and cooling to −15° the iodine compound was obtained as white crystals melting at 23.5°.

Twenty-four grams of α-iodo-α,β-dilaurin was refluxed on a water-bath in a mixture of 150 cc. of ethyl alcohol, 21 cc. of water and 24 g. of silver nitrite for one hour. After the separation of silver iodide, the reaction mixture was filtered hot. The filtrate was evaporated on a water-bath and left behind an oil mixed with silver compounds. The oil was taken up with 100 cc. of absolute alcohol, filtered and again evaporated. This time it was boneblacked to clear it. By slow evaporation of the alcohol the α,α-dilaurin crystallized in shining plates. After drying over phosphorus pentoxide in a vacuum desiccator the α,α-dilaurin melted sharply at 56.6'. Repeated crystallization did not change the melting point. The mother liquor crystals of the second recrystallization melted at 56.4–56.6°.

The following α,α-diglycerides were prepared in the above manner.

Compound	M. p., °C., found	Previously recorded
a,a-Dilaurin	56.6	55 (d), 57 (c), liquid (e)
α,α-Distearin	79.1	78.2 (c), 76.5 (f), 74.5 (g), 76 (a), 78.5–9 (h)
α,α-Dipalmitin	69.5	70 (a), 69 (b), 69.5 (i)
α,α-Dimyristin	63.8–64.4	61 (c), 63 (d)

(a) Ber., 38, 2285 (1905); (b) *Z. Biol.*, **44**, 88 (1913); (c) *Ber.*, 40, 1797 (1907); (d) ibid., 40, 1785 (1907); (e) Ber., 45, 3691 (1912); (f) **J.** ***prakt.*** *Chem.*, 28, 227 (1883); (g) *Z. Biol*, **44,** 78 (1903); (h) *Ber.*, 53, 1621 (1920); (i) *Biochem.* Z., 130, 252 (1922).

Synthesis of Triglycerides.—For the preparation of symmetrical mixed triglycerides the preparation of β-stearo-α,α-dilaurin is used as an example.

Four grams of α,α-dilaurin (1 mole) was dissolved in 5 cc. of chloroform and 1.42 g. (1.2 moles) of quinoline added. The flask containing this mixture was then placed in ice water and 2.9 g. (1.1 moles) of stearyl chloride in 2 cc. of chloroform was slowly added. After standing at room temperature for forty-eight hours, it was taken up with 300 cc. of ether and 100 cc. of ice-cold 0.5 N sulfuric acid and treated in the above manner for the separation of quinoline. After drying the solution over fused sodium sulfate, the ether was evaporated slowly, mostly at room temperature. The addition of alcohol to the chloroform remaining after evaporation of the ether caused a separation of the triglyceride. After drying over phosphorus pentoxide the glyceride melted at 49.8'. After two recrystallizations the melting point rose to 50.9' and was not changed by further crystallization.

For unsymmetrical mixed triglycerides, the monoglycerides were treated with two moles of an acyl halide and quinoline. The following triglycerides were prepared. Melting points and saponification numbers were taken as the best index of purity.

Compound	M. p., °C., found	Previously recorded
Trilaurin	45.6	45 (a), 45 (b), 46.4 (b)
β-Stearo-α,α-dilaurin	50.9	37.5 (e)
α-Stearo-α,β-dilaurin	45.4	46.0 (d)
β-Lauro-α,α-dimyristin	49.2–49.5	46.5 (e)
α-Lauro-α,β-dimyristin	48.5	45 (d)
6-Palmito-a,a-dimyristin	59.8–60.0	
α-Palmito-α,β-dimyristin	53.0	
β-Stearo-α,a-dipalmitin	64.8	59.1 (f), 63.3 (g), 60 (b)
α-Stearo-α,β-dipalmitin	62.6	63.5 (f), 60 (b)
6-Aceto-a,a-dipalmitin	54.0	49 (i)
α-Aceto-α,β-dipalmitin	51–52	67 (i)
β-Capro-α,α-dipalmitin	66.0	
α-Capro-α,β-dipalmitin	60.0	
β-Lauro-α,α-dipalmitin	63.5–64	
α-Lauro-α,β-dipalmitin	54.5	
β-Myristo-α,a-dipalmitin	58.5–59	
α-Myristo-α,β-dipalmitin	55.5	
β-Aceto-α,α-distearin	62.7	64.0 (c), 56.5 (e)

Compound	M. p., °C., found	Previously recorded
α-Aceto-α,β-distearin	56.6	69 (c), 44 (d)
α-Lauryl-α,β-distearin	50.9	49.5 (h), 49 (d)

(a) Ber., 45, 3691 (1912); (b) Lewkowitsch, 1921, Vol. I, 6th ed., p. 26; (c) Ber., 53, 1621 (1920); (d) ibid., 40, 1792 (1907); (e) ibid., 40, 1780 (1907); (f) Biochem. Z., 130, 252 (1922); (g) J. Chem. Soc., 129, 1458 (1926); (h) Ber., 53, 1589 (1920); (i) ibid., 38, 2284 (1905).

Discussion of Results

It is evident from the above data that there was a considerable difference in the melting points of many of the compounds previously prepared and those described in this work.

In the case of the previously recorded isomeric stearodipalmitins mixtures of the mono- or dipalmitins and fatty acid were heated. The positions of acyl groups in a mixed glyceride cannot be stated with certainty when using this procedure. Both recorded compounds showed melting points of 60° when prepared by this method. The use of high temperatures also accounts for the faulty results recorded for the acetodipalmitins and the acetodistearins. The reaction between acetic anhydride and α,α-diglycerides can be accomplished in the cold if pyridine is added.

Symmetrical stearodilaurin as prepared by Grün melts 13° below the compound reported here. He prepared it by the same method used here except that in his method no quinoline was used for the removal of hydrogen chloride and the mixture was heated. This type of reaction is incomplete and extensive shifting of the acyl groups takes place, giving a mixture of triglycerides. The same criticism holds for his symmetrical laurodimyristin, which he prepared by the same method and found to be mixed with other unidentified substances.

Many of the unsymmetrical triglycerides previously recorded in the literature, prepared from diacylchlorohydrins and soaps, are in good agreement with those reported here. It is to be noted, however, that the replacement of the chlorine does not take place smoothly and considerable amounts of by-products form, giving low yields. The following compounds prepared by this method agree with those prepared during the present investigation: α-laurodistearin, α,α-dilaurin, a-stearodilaurin, β-stearodipalmitin, a-monostearin, and trilaurin.

The simple triglycerides, trilaurin and trimyristin, both of which were prepared from the α,α-diglycerides using acyl chloride and quinoline, agree very well with the melting points of the same compounds recorded in the literature and prepared by other methods.

In several cases the mono- and diglycerides which were used in preparing the triglycerides recorded in the literature were from 3 to 5° lower in melting point than those herein reported.

In the nine sets of isomeric glycerides reported here the symmetrical isomer in each case was found to have the higher melting point. This was not the case in three of the five sets of isomers for which values could be found in the literature (acetodipalmitins, stearodilaurins and stearodipalmitins). The average difference in melting points between the symmetrical and unsymmetrical isomers for the nine sets prepared is 4.7°.

Fischer's methods have been used for the first time in the preparation of a-monocaprin, a-monomyristin, α,α-dilaurin, α,α-dimyristin and for the following sets of isomers: the stearodilaurins, acetodipalmitins, caprodipalmitins, laurodipalmitins, myristodipalmitins and the laurodimyristins. The caprodipalmitins, laurodipalmitins and myristodipalmitins had not been prepared previously.

Summary

1. The methods devised by Emil Fischer for the synthesis of unsymmetrical and symmetrical mixed glycerides have been extended to the preparation of glycerides not previously synthesized and used to recheck many of the data reported in the literature.

2. In rechecking data available for eleven triglycerides, differences between the melting points of the compounds previously prepared and those described in this work have been found. The differences are shown to be due to the methods of preparation used and the reasons for these differences are indicated.

3. The following new triglycerides have been prepared: the isomeric caprodipalmitins, laurodipalmitins, myristodipalmitins and palmitodimyristins.

4. In the synthesis of triglycerides, the following new intermediate compounds have been prepared: caprylacetoneglycerin, a-monocaprin, a-iododilaurin, a-iododimyristin.

5. It was found that the symmetrical isomer in each of the nine sets of isomeric triglycerides made had a higher melting point than that of the unsymmetrical isomer.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CIV. ISOURACIL AND ITS DERIVATIVES. A PRELIMINARY STUDY OF THE METHODS OF SYNTHESIS

BY TREAT B. JOHNSON AND W. T. CALDWELL[1]

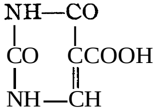
RECEIVED OCTOBER 26, 1928 PUBLISHED MARCH 6, 1929

The Constitution of Orotic Acid

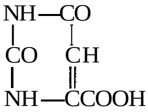
Various chemical aspects of the vitamin problem have stimulated an interest in the study of the chemistry of isouracil and its derivatives. Our interest in this type of pyrimidine compounds as possible vitamine constructions has been stimulated as a result of the continuation of some pyrimidine research which was inaugurated as early as 1907.[2] This research, which was of a preliminary nature, had to do with the question of determining whether orotic acid, $C_5H_4O_4N_2 \cdot H_2O$, is to be represented structurally as a pyrimidine compound.

Biscaro and Belloni[3] reported the isolation of this organic acid from milk whey in 1905 and described several of its derivatives. Sufficient experimental evidence was produced by these investigators to show that the acid is probably a heterocyclic compound having an ureide structure but insufficient data were obtained to enable them to draw a positive conclusion regarding its constitution.

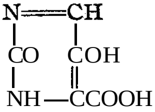
The properties of orotic acid suggested the possibility of its being a pyrimidine having the constitution of one of the uracil-carboxylic acids represented by Formulas I and II, respectively. Wheeler, Johnson and Johns[2] prepared the compound represented by Formula I, and later Wheeler[4] made a careful study of the isomeric pyrimidine II. Neither of these two pyrimidines possessed the specific properties which characterized the orotic acid described by Biscaro and Belloni. The non-identity of the two pyrimidines I and II with orotic acid being established, there now remained to be considered the third pyrimidine possibility, namely, isouracil-carboxylic acid represented by Formula III. The further study of this



I



II



III

---

[1] Constructed from a dissertation presented by William T. Caldwell, in June, 1923, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (T. B. J.)

[2] Wheeler, Johnson and Johns, *Am. Chem.* J.,37,392 (1907).

[3] Biscaro and Belloni, *Estratto dell'Annuario della Soc. Chimica di Mihno,* II, fasc. 1 (1905); Chem. *Zent*, *1,* 63, 64 (1905); II, fasc. 2 (1905).

[4] Wheeler, *Am. Chem.* J.,38, 358 (1907).

interesting problem has now introduced us to many new features of pyrimidine chemistry which promise to become of immediate biochemical interest. It is not improbable that the easiest approach to isouracil, $\overline{\mathrm{NCONHCH{=}C(OH)CH}}$, which is the only 2-oxypyrimidine isomeric with uracil, $\overline{\mathrm{NHCONHCH{=}CHCO}}$, will be by decarboxylation of isouracil-carboxylic acid, III. Tafel and Houseman[5] described what they believed to be two isomeric modifications of this pyrimidine but state that, in consequence of the fact that all attempts to rearrange one form into the other were unsuccessful, the formulas assigned were given with reservation. No method has yet been developed for the synthesis of an isouracil of known structure. This paper contains a preliminary account of new work in this field.

It is of interest to note at this time that Biscaro and Belloni also made a preliminary study of the physiological action of orotic acid. Injection of an aqueous solution of the potassium salt into a frog produced a violent excitation followed by a complete paralysis of the central nervous system. The same experiment repeated on guinea pigs with corresponding body doses produced less violent results, indicating, therefore, that orotic acid is apparently tolerated in some degree by warm-blooded animals. A remarkable property reported as characteristic of orotic acid is its specific affinity for potassium. The acid is said to be able to liberate hydrochloric and nitric acids in aqueous solutions of their respective potassium salts. The Italian investigators postulated that orotic acid is possibly a natural factor influencing the relative proportions of sodium and potassium found in the different fluids and in muscular tissues of the animal body. To date no exhaustive physiological examination of any pyrimidine-carboxylic acids has been carried on. In the light of the known physiological activity of the different carboxyl derivatives of pyridine and quinoline, for example, it seems not improbable that some of the carboxyl derivatives of the reduced forms of pyrimidine may prove interesting pharmacologically.

Our present research has been confined to the study of two different methods proposed for synthesizing carboxyl derivatives of isouracil. Neither of the two procedures studied has led thus far to practical results. In method one we started with ethyl diethoxy-acetoacetate[6] IV, and prepared the mercapto-pyrimidine V. This proved to be a compound characterized by very desirable properties and was easily converted into the pyrimidine VI by interaction with phosphorus pentachloride. By reduction of this halogen compound we were also successful in synthesizing 2-ethylmercapto-4-ethoxymethyl-5-ethoxypyrimidine VII, which on hydrolysis apparently yields smoothly 2-oxy-4-ethoxymethyl-5-ethoxypyrimi-

[5] Tafel, *Ber.*, 34,258 (1901); Tafel and Houseman, *Ber.*, 40,8743 (1907).

[6] See Johnson and Hadley, THIS JOURNAL, 38, 1850 (1916).

dine VIII. The method of operating, involving as it does so many steps, does not yield this pyrimidine, however, in sufficient quantity to proceed through the last two steps of the synthesis represented by Formulas IX and III.

An interesting pyrimidine obtained in our research was the alcohol represented by either of the two formulas, X and XI. This proved to be very resistant to the action of hydrochloric acid, a result quite in accord with the behavior of other alcohols of this type in the uracil series.[7]

IV $C_2H_5OCH_2COCH(OC_2H_5)COOC_2H_5$

V $\overline{NHC(SC_2H_5){=}NC(CH_2OC_2H_5){=}C(OC_2H_5)CO}$

VI $\overline{NC(SC_2H_5){=}NC(CH_2OC_2H_5){=}C(OC_2H_5)CCl}$

VII $\overline{NC(SC_2H_5){=}NC(CH_2OC_2H_5){=}C(OC_2H_5)CH}$

VIII $\overline{NCONHC(CH_2OC_2H_5){=}C(OC_2H_5)CH}$

IX $\overline{NCONHC(CH_2OH){=}COHCH}$ X $\overline{NHCONHC(CH_2OH){=}C(OH)CO}$

XI $\overline{NHCONHCH(CH_2OH)COCO}$

In method two the starting point was the compound ethyl oxalo-ethoxyacetate, XII. This was found to interact with pseudo-ethylthiourea with formation of the pyrimidine XIII, but less favorably than the ketone ester IV under similar conditions. This observation is quite in accord with that of Wheeler,[8] who failed to obtain mercapto-pyrimidines by condensing pseudothioureas with ethyl oxalo-acetate. On the other hand, Johnson[9] found that ethyl oxalopropionate condenses smoothly with pseudothioureas. The pyrimidine XIII is converted by hydrolysis in hydrochloric acid solution into its corresponding diethoxy derivative, XIV, the mono-ethoxy compound, XV, and finally to isobarbituric acid XVIII with loss of carbon dioxide. It has been found also that the mercapto-pyrimidine XIII interacts normally step by step (XVI ⟶ XVII ⟶ III) up to the last stage of the synthesis, but not until we have found more favorable experimental conditions for the pseudothiourea condensation will it be practicable to apply this method of synthesis for the production of isouracil-carboxylic acid, III, in quantities needed for our researches.

XII $C_2H_5OOCCOCH(OC_2H_5)COOC_2H_5$

XIII $\overline{NHC(SC_2H_5){=}NC(COOC_2H_5){=}C(OC_2H_5)CO}$

XIV $\overline{NHCONHC(COOC_2H_5){=}C(OC_2H_5)CO}$

XV $\overline{NHCONHC(COOH){=}C(OC_2H_5)CO}$

---

[7] Johnson and Chernoff, THIS JOURNAL, 35, **585** (1913); see Kircher, Ann., **385**, 293 (1911).

[8] Wheeler, *Am. Chem. J.*, **38**, **358** (1907).

[9] Johnson, *J. Biol. Chem.*, **3**, 299 (1907).

XVI $NC(SC_2H_5)=NC(COOC_2H_5)=C(OC_2H_5)CCl$

XVII $NC(SC_2H_5)=NC(COOC_2H_5)=C(OC_2H_5)CH$ XVIII $NHCONHCH=C(OH)CO$

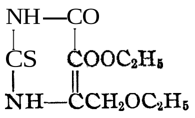
III $NCONHC(COOH)=COHCH$

Biscaro and Belloni state that orotic acid fuses with decomposition at 260". As to whether this is a sharp and definite decomposition point we have no knowledge, but it is an interesting fact that the acid III, obtained by us according to the second outlined method of synthesis, melted with decomposition at the same temperature, 259–260°.

A complete record of our experimental work is given in the final section of this paper. This investigation is being continued by other co-workers in this Laboratory.

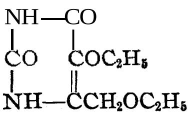
Experimental Part

2-Thio-4-ethoxymethyl-5-ethoxy-6-oxypyrimidine.—This pyrimidine was prepared by condensing thiourea with ethyl α,γ-diethoxyacetoacetate as follows: 7.6 g. of thiourea and 21 g. of ethyl α,γ-diethoxyacetoacetate were added to a solution of sodium alcoholate made by dissolving 2.3 g. of metallic sodium in 75 cc. of absolute alcohol. The resulting mixture was then refluxed in an oil-bath for eight hours, during which time the liquid changed in color from orange to dark red. On cooling, needle-shaped crystals separated from the solution. The alcohol then was distilled off under diminished pressure and the residue dissolved in 100 cc. of water and made acid to litmus with hydrochloric acid. Crystals of the pyrimidine separated and were purified by recrystallization from water after decolorizing with animal charcoal. The thiopyrimidine is practically insoluble in cold water and requires about 100 parts of boiling water for solution. It crystallizes in colorless needles, giving strong tests for nitrogen and sulfur, and melts at 178°.



Anal. Calcd. for $C_9H_{14}O_3N_2S$: N, 12.17. Found: N, 12.28, 12.29.

2-Oxy-4-ethoxymethyl-5-ethoxy-6-oxypyrimidine.—This pyrimidine was obtained from the corresponding thio-compound by the action of chloro-acetic acid. 2.53 g. of the above thiopyrimidine was treated with 3.16 g. of chloro-acetic acid in 60 cc. of distilled water and the mixture refluxed for five hours. On cooling, the 2-oxypyrimidine separated in large crystals and melted to a colorless liquid at 168°. The yield was 1.93 g., or 82% of the theoretical. The sulfur from the thiopyrimidine remained in the mother liquid combined in the form of thioglycolic acid, as shown by the characteristic and beautiful color test with ferric chloride and ammonia.



Anal. Calcd. for $C_9H_{14}O_4N_2$: N, 13.08. Found: N, 13.13.

2-Oxy-4-hydroxy-5-hydroxy-6-oxypyrimidine, IX.—0.92 g. of the above pyrimidine was placed in a pressure tube with 10 cc. of concentrated hydrochloric acid, sealed and heated for two hours at 120–140°. After cooling, the tube was opened and the gas which escaped burned with a green flame; the odor of ethyl chloride was noticeable. Before heating, the pyrimidine dissolved in the hydrochloric add, forming a clear solution; during the reaction the liquid became bright yellow and a yellow precipitate separated which was practically insoluble in water. This was digested with distilled water, filtered off and dried at 100°. The yield was 0.63 g., or 93% of the theoretical. The substance burned up completely when ignited on platinum foil. It did not melt when heated to 320'.

And. Calcd. for $C_5H_6O_4N_2$: N, 17.72. Pound: N, 17.61.

2-Ethylmercapto-4-ethoxymethyl-5-ethoxy-6-oxypyrimidine, V.—This compound was prepared by adding 20 g. of pseudo-ethylthiourea hydrobromide to a solution of 20 g. of ethyl α,γ-diethoxyacetoacetate in water containing 10 g. of sodium hydroxide. The mixture was then heated on the water-bath, upon which it became darker in color and ethyl mercaptan was evolved. After heating for eight hours the solution was cooled and acidified, giving a dark colored and rather oily mixture which was set aside to crystallize. This process was slow in starting but on long standing there separated dark colored, but very well formed, stocky crystals. These were purified by recrystallization from alcohol and decolorization with animal charcoal, when they were obtained in colorless crystals. The yield of the purified product was 4 g. The pyrimidine was practically insoluble in water but soluble in alcohol and acetone and gave good tests for nitrogen and sulfur. It melted at 123°.

Anal. Calcd. for $C_{11}H_{18}O_3N_2S$: N, 10.85. Found: N, 10.99, 10.91.

This compound was also obtained in the following way without first isolating the ketone ester; in general this latter method was preferable: 8.7 g. of metallic sodium in small pieces was added directly to 100 *g.* of ethyl ethoxyacetate in a dry flask connected with a reflux condenser. After cooling during the first stage of the reaction, the flask was suspended in a water-bath and heat applied until all of the sodium had dissolved. Then 70 g. of pseudo-ethylthiourea hydrobromide in absolute alcohol was added to the crude condensation product, the mixture warmed on the water-bath and then set aside to stand at room temperature. The formation of crystals in the dark-colored, viscous liquid was very slow in starting; alcohol and acetone were added in order to thin the material and the whole was then allowed to stand. During this time the crop of crystals gradually increased; after purification they were obtained in white, crystalline form, melting sharply at 123°. The yield was 14 g.

2-Ethylmercapto-4-ethoxymethyl-5-ethoxy-6-chloropyrimidine, VI.—9.53 *g.* of finely powdered phosphorus pentachloride was added to 11.7 g. of 2-ethylmercapto-4-ethoxymethyl-5-ethoxy-6-oxypyrimidine contained in a dry flask attached to a reflux condenser. After thorough mixing, no reaction was apparent after standing at room temperature for half an hour. The mixture was then moistened with *2* cc. of phosphorus oxychloride, forming a thick paste with a light yellow color but causing no further reaction. After half an hour the color was still unchanged, so the mixture was heated in a water-bath until the temperature rose to 80°, when the reaction started. With brisk evolution of hydrogen chloride an orange-red liquid was formed, but no odor of mercaptan was noticed. This liquid rapidly became darker in color; after fifteen minutes the water was raised to the boiling point and the heating continued for two hours. After the evolution of hydrogen chloride had ceased, the phosphorus oxychloride was distilled off on the water-bath under diminished pressure. The residue was treated with crushed ice, then warmed gently, neutralized with successive portions of ether and the solution placed over calcium chloride to dry.

The ethereal extract was then heated to remove ether and the residue of oil distilled under diminished pressure. It boiled at 165–166° under a pressure of 9–10 mm., distilling as a light yellow oil which did not solidify on cooling to 0°. The substance had an odor very suggestive of naphthalene. The yield was 7 g.

This pyrimidine also was prepared by allowing the reaction to take place in chloroform solution: 6.52 g. of the pyrimidine was dissolved in 50 cc. of chloroform and treated with 5.25 g. of phosphorus pentachloride dissolved in 66.7 cc. of chloroform. After refluxing for an hour the liquid changed from yellow to dark green in color. Five cc. more of the chloroform solution of phosphorus pentachloride was added in order to give a slight excess of this reagent and the heating continued for several hours, during which time the liquid became brown. The chloroform then was removed and the residue worked up from this point as in the previous case, the pyrimidine being obtained as an oil, insoluble in water.

Anal. Calcd. for $C_{11}H_{17}O_2N_2SCl$: Cl, 12.81. Found: Cl, 12.90.

2-Ethylmercapto-4-ethoxymethyl-5-ethoxypyrimidine, VII.—The 6-chloropyrimidine described above was dissolved in 115 cc. of alcohol and 75 cc. of water. This solution then was boiled under a reflux condenser with 35 g. of 87% zinc dust that was added in portions in the course of two hours. This liquid then was filtered from the residual zinc while hot, washing well with fresh alcohol. The solvent was removed by warming under diminished pressure until but a small quantity of water remained, containing a heavy red oil. This was extracted with ether and dried over calcium chloride.

The ether was distilled from the ethereal solution and from the residue there separated small crystals, which were first washed with alcohol to free them from adhering oil, finally with ether and petroleum ether and further purified by recrystallization from alcohol. The pyrimidine separated in the iorm of plates and gave good tests for both nitrogen and sulfur but not for chlorine and melted sharply at 167° to a clear oil.

Anal. Calcd. for $C_{11}H_{18}O_2N_2S$: N, 11.57. Found: N, 11.58. Mol. wt. (boiling point method using benzene as solvent). Calcd.: 242. Found: 244.

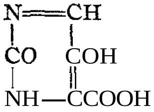
On hydrolysis of a small amount of the above pyrimidine with hydrochloric acid, ethylmercaptan was evolved and we obtained crystals of a substance which darkened very considerably at 281–284° with vigorous effervescence and decomposition. As little material was available this was not investigated but it was very probably 2-oxy-ethoxymethyl-5-ethoxypyrimidine.

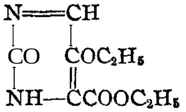
2-Ethylmercapto-4-ethylcarboxylate-5-ethoxy-6-oxypyrimidine, XIII.—Thirty-seven g. of freshly distilled ethyl oxalate and 33 g. of ethyl ethoxyacetate were dissolved in 100 cc. of anhydrous ether and placed in a dry flask attached to a reflux condenser. Then 5.75 g. of metallic sodium in wire form was added. After completion of the condensation with disappearance of the sodium, 41 g. of pseudo-ethylthiourea hydrobromide was added. The liquid emulsified and became yellow in color. It was warmed on the water-bath in order to distil off most of the ether, during which time the color became deeper; upon adding a solution of 14 g. of potassium hydroxide in alcohol to this, solid material began to collect in the flask and the liquid became darker in color. The mixture was then warmed on the water-bath for half an hour and in an oil-bath at 110–120° for two hours, during which time mercaptan was constantly evolved and the color became a deep brown. On cooling, a thick, almost solid, dark-colored mass remained. This was treated as follows: fifteen grams of glacial acetic acid was added in portions, the mixture warmed with 50 cc. of water and then cooled in ice. The crystals and semi-solid material which separated were filtered off and triturated with cold water. when we succeeded in obtaining a colorless product in the form of needles. This was purified by recrystallization from boiling water containing animal charcoal and dried in a vacuum desiccator. The substance gave strong tests for both nitrogen and sulfur and melted at 82–83°. The yield of this pyrimidine was small, but the condensation reaction leading to its formation is promising of further development and it will be studied exhaustively, as this combination would make possible many interesting syntheses if it were available in quantity. Its investigation will be continued.

Anal. Calcd. for $C_{11}H_{16}O_4N_2S$: N, 10.29. Found: N, 10.03.

That this pyrimidine behaves normally and is a stable construction was evidenced by its reactivity with phosphorus oxychloride: 0.5 g. was treated with 2 cc. of the oxychloride, whereupon the compound dissolved immediately. Hydrogen chloride was evolved and a clear solution was obtained after heating for half an hour on the water-bath. The excess of oxychloride then was removed by warming on the water-bath under diminished pressure. After adding ice and gently warming the mixture it was made neutral to litmus with dilute potassium hydroxide. On extracting with ether and evaporating the solvent, a red oil was obtained which contained both chlorine and sulfur and was undoubtedly mercapto-4-ethylcarboxylate-5-ethoxy-6-chloropyrimidine. As no micro-chemical apparatus was available it was impossible to obtain any analytical determinations confirming this constitution.

In order to determine whether this chloropyrimidine is easily reducible, all the material available was dissolved in 20 cc. of absolute alcohol and reduction applied by boiling with zinc dust under a reflux condenser for three hours after adding **10** cc. of water. The dark red color soon disappeared, the supernatant liquid becoming light yellow, almost colorless. After filtering off the zinc, the filtrate was evaporated and extracted with ether. On evaporating the ether a light yellow oil was obtained which finally solidified in the form of hexagonal plates melting at 55–56°. This compound was free from chlorine and its low melting point indicated that we were dealing with the new pyrimidine, 2-ethylmercapto-4-ethylcarboxylate-5-ethoxypyrimidine. It gave a strong test for sulfur. When this compound was heated at 120° with 10 cc. of hydrochloric acid, ethylmercaptan was evolved, showing that the original mercapto grouping had not been destroyed by the previous treatment with phosphorus oxychloride and zinc. The liquid in the bomb tube was yellow in color. On concentrating the acid solution and cooling, a beautiful crystalline substance separated in the form of prisms which melted at 259°. Whether we are dealing here with 2-oxy-4-carboxyl-5-hydroxypyrimidine (orotic acid?) or its corresponding diethyl derivative remains to be determined by further work.





2-Oxy-4-ethylcarboxylate-5-ethoxy-6-oxypyrimidine, XIV.—Thirty-six g. of ethyl oxalethoxyacetoacetate was mixed with a solution of **30** g. of pseudo-ethylthiourea hydrobromide in water. To this was added **15** g. of sodium hydroxide dissolved in water. After standing overnight the mixture was heated on the boiling water-bath, cooled and acidified with hydrochloric acid, whereupon a large amount of mercaptan was evolved from the dark-colored mixture. As it was difficult to stimulate crystallization of any of the products of the condensation, the material was set aside and allowed to stand. From the crystals that ultimately separated this pyrimidine was isolated and purified by several recrystallizations from water, in which it was only moderately soluble. After decolorizing with animal charcoal, it was obtained in the form of colorless needles. It gave no test for sulfur and melted at 230°.

Anal. Calcd. for $C_9H_{12}O_5N_2$: C, **47.36;** H, **5.3;** N, **12.28.** Found: C, 47.68; **H, 5.77; N, 12.07.**

2-Oxy-4-carboxylic **Acid** 5-Ethoxy-6-oxypyrimidine, **XV.**—This compound was obtained along with the pyrimidine just described, from which it was separated by fractional crystallization from alcohol and water. It is practically insoluble in cold water, from which it separates in hexagonal crystals melting sharply at 260° with decomposition. Some of the same pyrimidine was obtained in one experiment in which thiourea and oxalethoxyacetoacetic ester were allowed to react in alcohol containing sodium alcoholate. In this case the reaction product stood for a long time after acidification with hydrochloric acid before the pyrimidine was isolated.

Anal. Calcd. for $C_7H_8O_5N_2$: C, 42.0; H, 4.0; N, 14.0. Found: C, 42.18, 42.4; H, 4.51; N, 13.27, 13.18.

2,6-Dioxy-5-hydroxypyrimidine (Isobarbituric Acid), XVIII.—One g. of 2-oxy-4-carboxylic acid 5-ethoxy-6-oxypyrimidine was sealed in a tube with 10 cc. of concentrated hydrochloric acid and heated for two hours at 110°. Under these conditions no reaction took place. It was therefore heated again for ten hours at 160–165°. The reaction product was found to be insoluble in water and also difficultly soluble in alcohol. On recrystallization from alcohol it separated in the form of microscopic crystals arranged in clusters. These decomposed without melting at 350–355°. The compound was identified as isobarbituric acid. In other words, the carboxyl group is removed by intensive hydrolysis, the pyrimidine behaving in an entirely different manner than uracil-4-carboxylic acid,[2] which resists hydrolysis when heated with 20% sulfuric acid at 200°.

Anal. Calcd. for $C_5H_4O_5N_2$: N, 16.27; for $C_4H_4O_3N_2$: N, 21.87. Found: N, 21.71.

Summary

1. Isouracil-carboxylic acid can exist theoretically in several isomeric modifications and is isomeric with *orotic* acid, a substance stated to have been isolated from milk by Biscaro and Belloni.
2. Experimental evidence has been obtained indicating that isouracil-carboxylic acid may be identical with orotic acid.
3. Two different methods of synthesis have been applied for preparing isouracil-carboxylic acid. Only one thus far gives promise of leading successfully to this pyrimidine.
4. Several new derivatives of isouracil have been prepared.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF MISSOURI]

THE SEPARATION OF THE SOLUBLE PROTEINS OF RABBIT MUSCLE

BY WALTER S. RITCHIE AND ALBERT G. HOGAN

RECEIVED OCTOBER 27, 1928 PUBLISHED MARCH 6, 1929

The earlier work on the separation of muscle proteins has been adequately reviewed,[1] so we will omit a detailed report of those investigations. Howe[2] has recently described a very ingenious procedure which deserves further study, in order to define more precisely the limits of its usefulness. There are several other recent papers[3] that have some bearing on the problem of extracting and separating muscle proteins, though they do not con-

---

[1] G. Mann, "Chemistry of the Proteids," Macmillan and Co., London, 1906.

[2] Howe, *J. Biol. Chem.*, **61**, 493 (1924).

[3] Lloyd, *Proc. Roy. Soc. London*, **89B**, 277 (1916); Collip, *J. Biol. Chem.*, **50**, xlv (1922); Granstrom, *Biochem. Z.*, **134**, 589 (1922); Weber, *ibid.*, **158**, 443 (1925); **184**, 407 (1927); Salter, *Proc. Soc. Exptl. Biol. Med.*, **24**, 116 (1926); Wohlisch and Schriever, *Z. Biol.*, **83**, 265 (1925).

tribute directly to our knowledge of the quantities that may be obtained. Lack of space, however, prevents more than mere mention.

Experimental

For our preliminary observations it seemed necessary to have samples that were as uniform as could be obtained. The material should be readily available, the tissue should be fresh and reasonably free from blood, so rabbits were chosen as experimental animals. They were killed by striking them a sharp blow on the back of the neck and the posterior portion of the animal was perfused with a Ringer-Locke solution until the perfusing liquid was free from color. At this point the rabbit was quickly skinned, the hind quarters removed and the tissue needed separated from the bone. We have assumed that complete removal of the soluble muscle proteins cannot be accomplished unless the tissue is finely subdivided, and have used two methods of grinding, either of which we regard as at least fairly satisfactory. When we first began, the samples were frozen with carbon dioxide and ground in a mortar. A somewhat higher percentage of extraction was obtained when samples were ground in this way but the procedure was tedious, and as the degree of extraction was not of primary importance at the time, this method of grinding was discontinued. Samples were next ground in a Nixtamal mill, which gives a very finely divided sample.

Methods of Extraction.—The samples, either 100 or 125 g. in size, were equally divided between four bottles of 200-cc. capacity and 100 cc. of the extracting solution was added to each bottle. These were gently shaken and allowed to stand for about an hour. The bottles were then centrifuged until the solid material had been thrown down making it possible to pour off the supernatant liquid without loss of tissue and the procedure was repeated until we were ready to discontinue extraction. When the extraction was complete the extract was made to volume, 2.0 liters for a 100-g. sample, 2.5 liters for a 125-g. sample, and filtered through a dry pad of cellucotton on a Büchner funnel. It has been reported frequently that muscle albumin rapidly changes its properties if allowed to stand at ordinary temperatures. For that reason the original samples, and all extracts, were constantly kept packed in a mixture of ice and salt. Nitrogen was determined in the original sample of muscle and in aliquots of the extract.

In studies such as we are reporting the choice of a solvent is of considerable importance, so we tried a large variety of solutions. Some of these were promising, but for various reasons we decided to use only 10% sodium chloride. It uniformly yielded a percentage extraction as high or higher than the other solutions, with the exception of ammonium chloride. In addition we had in mind the possibility of studying the separated proteins by the use of titration curves, and we wished to use a salt that has no buffer action. The hydrogen-ion concentration of the extracting solution was adjusted to a P_H value of about 6, varying between 5.9 and 6.1. The electrometric method was used almost exclusively in making hydrogen-ion determinations.

Separation of Protein.—In our studies of the forms of nitrogen present in muscle extracts, we have considered only three fractions, designated by us as albumin, globulin and non-protein nitrogen. In our preliminary observations various methods of precipitating the globulin were tried. Several of these offer promise but we are only reporting three in any detail: salting-out, dialysis and irradiation with a quartz mercury arc.

As to the salting-out process, several different salts seemed suitable for the purpose and our final choice of sodium chloride was based chiefly on convenience. An additional reason was that the same salt had been used as the solvent.

During our efforts to develop a satisfactory technique for precipitation by dialysis, we attempted the method of electro-dialysis. At first this procedure was regarded as very promising, but it was soon discarded, due to the difficulty of controlling the hydrogen-ion concentration. We finally decided to try dialysis by the usual method, taking such precautions as we might to prevent changes in the solubility of the protein. The dialyzing cell was immersed in ice water and toluene and thymol were added to prevent bacterial action. We believe these precautions are largely effective.

So far as we are aware, exposure to ultraviolet rays has never been used as a method of precipitating proteins quantitatively, though the effect of rays of short wave length on proteins has been reported by a number of investigators. Most of the publications have been reviewed by Clark[4] and by Stedman and Mendel[5] and we are omitting any discussion of individual reports. These contain many discrepancies but there is almost complete agreement on one point: protein solutions are rendered more unstable by irradiation. Some proteins are much more affected than others; for example, albumins are less readily coagulated by irradiation than are globulins. It occurred to us that if our muscle extracts contain two proteins, one might be coagulated more quickly than the other and so separated more or less quantitatively. We made no effort to determine whether or not the effects observed were due entirely to ultraviolet rays. The work of Young[6] suggests that visible rays also may bring about marked changes in the properties of protein solutions.

Precipitation of Muscle Globulin by Saturation with Sodium Chloride.—Since albumins in a concentrated salt solution are precipitated by the addition of acid, it seemed advisable first to determine within what range of hydrogen-ion concentration the globulin could be precipitated without contamination with albumin. Apparently the same amount of protein is precipitated at a P_H of 6, 7 or 8. Distinctly larger amounts are precipitated at a P_H of 5. Prom the standpoint of convenience in manipulation, a P_H of 6 is to be preferred, as the precipitate is always granular in character and easily washed on the filter. At a P_H of 7 the precipitate is slightly gelatinous at times, and at a P_H of 8 it is distinctly slimy and the washing process is very slow. The procedure of salt separation is well known, so we are omitting details of the technique we employed. Typical results are given in Table I.

[4] Clark, *Am. J. Physiol.*, *73*, 649 (1926).

[5] Stedman and Mendel, ibid., 77, 199 (1926).

[6] Young, *Proc. Roy. Soc. London*, 93B, 235 (1922).

TABLE I

PROTEIN IN EXTRACT PRECIPITATED BY SATURATION WITH SODIUM CHLORIDE

Date	P_H				
	4	5	6	7	8
12/29/26			61.3	56.3	
1/28/27	80.7	85.9	62.3	59.7	59.7
2/23/27	82.8	79.4	60.3	61.8	64.0
3/15/27	75.3	70.8	60.6	51.2	52.7
4/ 4/27	84.3	77.5	61.8	57.8	62.1
4/18/27		78.1	59.4	57.7	
5/10/27		73.8	57.7		
6/ 1/27		80.7	60.8		
9/28/27		80.1	61.4	57.3	
10/17/27		65.6	59.3	50.1	
12/10/27		69.2	56.7	54.5	
12/30/27		78.1	60.9	61.1	
1/30/28		69.3	53.3	53.3	

Separation of Globulin by Dialysis.—Parchment chambers were used for dialyzing cells and in practically every case four aliquots were taken. They were dialyzed against tap water for twenty-four hours, against distilled water for twenty-four hours and then for another twenty-four hours against distilled water of a definite hydrogen-ion concentration. In terms of P_H units these were 4, 5, 6 and 7. After dialysis was complete, the precipitate was used for a nitrogen determination; also, an aliquot of the filtrate was saturated with sodium chloride and the nitrogen content of the precipitate was determined. The sum of these determinations was taken as representing the total globulin. We have explained the possible presence of globulin in the filtrate by assuming that it is held in solution by the albumin or by the non-protein constituents. After dialysis the solution does not give a test for chlorides.

The amount of protein precipitated seemed to be unrelated to the hydrogen-ion concentration of the dialysate, for the amount of protein precipitated in the four cells was approximately the same. There was considerable variation in individual determinations, however, as is shown in Table II.

TABLE II

PROTEIN IN EXTRACT PRECIPITATED BY DIALYSIS

P_H	Date							
	2/23/27	3/15/27	4/4/27	4/18/27	5/10/27	10/17/27	12/10/27	1/30/28
4	50.2	54.0	58.9	58.8	64.6	52.2	60.4	63.2
5	51.2	53.3	53.4	60.9	58.7	54.4	64.8	64.7
6	..	50.6	65.8	59.9	55.9	57.5	67.7	66.3
7	48.0	53.1	57.6	55.8	57.6	57.3	..	66.0

Precipitation by Exposure to Ultraviolet Rays.—A preliminary trial made it quite evident that protein is precipitated from solution by irradiation with a quartz mercury arc, so we attempted to determine whether the method could be used for the quantitative estimation of muscle globulin. Our experience was that the hydrogen-ion concentration of the liquid had to be controlled quite rigidly if precipitation by irradiation was to be satisfactory. At a P_H of 4 or 5 the quantity of protein precipitated was definitely too high. Best results were obtained at a P_H of approximately 6, as precipitation was quite rapid and the precipitate was flocculent and easily washed. At a P_H of 7 or 8 a longer time was required for precipitation and the precipitates were too gelatinous to be filtered and washed satisfactorily. In order to obtain more definite information as to the time required for precipitation, extracts at a P_H of 5.8 were exposed for variable periods of time, one, two, four, six and eight hours. It developed that irradiation for four hours or less is too short a period, and that the quantity of protein precipitated during six or eight hours is about the same.

Determination of Albumin.—The filtrates obtained by the three different procedures for globulin precipitation varied widely in their salt content but all were treated alike for the precipitation of the albumin. They were heated to boiling and sufficient trichloro-acetic acid was added to make the final concentration 2.5%. The nitrogen content of the precipitate was then determined.

Determination of Non-Protein Nitrogen.—The filtrates from the albumin precipitates were taken for nitrogen determinations. This fraction was designated as non-protein nitrogen.

Comparison of Procedures.—Thus far our chief effort has been to obtain evidence that would justify the use of the three methods mentioned, saturation with sodium chloride, dialysis and irradiation with ultraviolet rays. A more critical test of the value of the procedures we have followed is to compare all three of them when applied to the same sample. Our data are tabulated to show such a comparison in Table III.

Inspection of Table III shows that the quantity of globulin precipitated by the three methods agrees within reasonable limits. At a P_H value of approximately 6 all methods give about the same result. Dialysis consistently gives slightly lower results than the other methods, possibly for the reasons mentioned in an earlier paragraph.

Little need be said concerning the albumin determinations, for they obviously depend on the amount of protein estimated as globulin. As a matter of fact the chief value of determinations of albumin and non-protein nitrogen is as a check on the accuracy of the analytical procedures.

We have not made an intensive study of the method of heat separation but, as this procedure may prove useful, we are including a statement of our experience.

Aliquots of the sodium chloride extract (usually 25 cc.) were transferred to 50-cc. centrifuge tubes, then placed in a water-bath maintained at 49°. When the protein solution reached this temperature it was allowed to

TABLE III

A COMPARISON OF THE PROCEDURES USED FOR THE SEPARATION OF MUSCLE PROTEIN

		Method of separation				
		Saturation with NaCl		Irradiation,	Dialysis,	Heat and trichloroacetic
Date	Substance	Px 6, %[a]	P_H 7, %	P_H 6, %	%	acid, %
4/ 4/27	Globulin	61.8	57.8	54.7	68.7	80.8
	Albumin	20.5	25.1	17.1	12.4	
	Non-protein nitrogen	16.8		27.4	7.5	20.4
4/18/27	Globulin	59.4	57.7	55.7	56.0	82.1
	Albumin	23.9	24.6	16.9	21.3	
	Non-protein nitrogen	7.9	9.7	27.4	9.1	18.5
9/28/27	Globulin	61.4	57.8	53.8	43.5	84.5
	Albumin	27.1	25.6	29.9	22.0	
	Non-protein nitrogen	18.8	18.3	21.8	8.5	19.3
10/27/27	Globulin	59.3	50.1	42.3	46.1	83.5
	Albumin	28.3	30.8	43.5	20.9	
	Non-protein nitrogen	17.5	16.7	20.0	11.3	19.0
1/30/28	Globulin	51.3	51.3	57.3	52.3	78.0
	Albumin	23.5	20.1	21.3	16.9	
	Non-protein nitrogen	22.0	22.3	19.5	13.8	19.7

[a] All percentages are in terms of the extracted nitrogen.

remain until the precipitate was in a flocculent condition and the filtrate was clear. The time required varied from fifteen to twenty minutes. Our results are summarized in Table IV.

TABLE IV

SEPARATION OF MUSCLE PROTEINS BY HEAT COAGULATION

Date	2/24/24	4/23/24	5/21/22	7/2/24	7/12/24	7/18/24
Globulin	51.9	50.9	55.7	54.9	47.5	48.5
Albumin	28.3	16.1	25.3	18.4	19.6	22.0
Non-protein N	19.3	31.2	20.6	26.5	28.4	26.1
Date	**7/28/24**	**10/5/24**	**10/9/24**	**11/22/24**	**1/28/28**	**2/13/25**
Globulin	57.2	60.7	64.3	57.6	63.2	60.1
Albumin	19.5	22.2	25.6	33.3	18.7	28.9
Non-protein N	24.1	19.0	13.7	9.8	15.5	16.5

The ratio of globulin to albumin as estimated by our methods is uniformly about 2.5 to 1 and is not in agreement with most of the earlier reports. Thus Streyrer[7] and Saxl[8] both reported considerably more albumin than globulin. Mann[9] in his discussion of this subject says that myogen (albumin) makes up about 80% of muscle albumin. On the other hand, Stewart and Sollman[10] report that paramyosinogen (globulin) is more abundant than myosinogen (albumin).

At various times measurements were made of the hydrogen-ion concen-

---

[7] Steyrer, *Beitr. chem. Physiol. Path.*, 4,234 (1904).

[8] P. Saxl, *ibid.*, 9, 1 (1907).

[9] Mann, "Chemistry of the Proteids," Macmillan and Co., London, 1906, p. 389.

[10] Stewart and Sollman, J. *Physiol.*, 24, 427 (1899).

tration of the filtrates from the globulin precipitates. We regard these measurements, Table V, as of some interest though they may have no immediate application to our problem.

TABLE V

CHANGE IN HYDROGEN-ION CONCENTRATION AFTER PRECIPITATION OF THE GLOBULIN

Initial PH of extract	4	5	6	7
After saturation with NaCl	4.4 4.4 4.1	4.8 5.3 5.2	5.9 5.8 6.0	6.7 6.7 6.6
	4.3	4.6 5.1 4.8	5.7 5.7 5.7	6.5 6.4 6.7
		4.7 5.3	5.7 5.9	6.7
After dialysis	7.4 7.9 7.5	7.4 7.8 7.1	7.5 7.9 7.5	7.6 7.2 7.9
	6.4 7.0 7.5	6.4 8.4 8.0	6.6 8.3 7.6	6.7 7.6 6.9
	6.3	6.7	6.9	
After irradiation with ultra-violet rays	Ten filtrates shifted from a PH of approximately 5.7 to a PH that varied between 6.8 and 7.			

When globulin was precipitated by saturation with sodium chloride, the PH values were shifted in some cases toward a point between 4 and 5, in others toward a point between 5 and 6. After dialysis the solutions were practically always more alkaline than the distilled water against which they were finally dialyzed.

Measurements of the hydrogen-ion concentration of irradiated solutions were not made unless the globulin was precipitated in a flocculent condition. In such cases the initial PH value was usually a little less than 6, and such solutions always become more alkaline. Our experience agrees with that of Clark[11] who noted that the PH of irradiated solutions increased. Mond[12] observed that the PH shifted toward the isoelectric point. Stedman and Mendel[13] observed that their solutions always became acid, but suggested that this shift was due to the effect on the solvent rather than to any change that occurred in the protein.

Summary

A 10% solution of sodium chloride has been used to extract the soluble proteins of muscle tissue. If the extract is kept near the freezing point the solubility of the proteins changes very slowly.

When the extract is saturated with sodium chloride, irradiated with a quartz mercury arc or dialyzed, a portion of the protein is precipitated, to approximately the same extent by each method. We have assumed that this precipitate is a globulin fraction. Our results indicate that this extract contains about 2.5 times as much globulin as albumin.

Columbia, Missouri

---

[11] Clark, *Am. J. Physiol.*, 73,649 (1925).

[12] Mond, *Pflüger's arch. ges. Physiol*, 200, 374 (1923).

[13] Stedman and Mendel, *Am. J. Physiol.*, 77, 199 (1926).

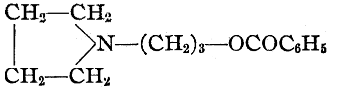
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

GAMMA-PYRROLIDINO- AND GAMMA-PYRROLINOPROPYL BENZOATES[1]

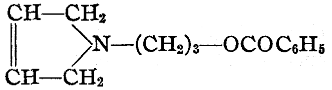
BY LESLIE H. ANDREWS AND S. M. MCELVAIN

RECEIVED OCTOBER 29, 1928 PUBLISHED MARCH 6, 1929

In a previous communication[2] the preparation of a number of substituted piperidino-alkyl benzoates was described. A preliminary pharmacological report on these substances indicated that they possessed local anesthetic action, the compounds in which a methyl group was substituted in the piperidine nucleus being the most efficient pharmacologically. The original purpose of the work which is reported in this paper was to prepare and submit for pharmacological study a corresponding series of compounds containing the pyrrolidine nucleus instead of the piperidine nucleus. However, on account of certain difficulties that are mentioned below, the substituted pyrrolidino-alkyl benzoates have not been prepared as yet, but two new substances, γ-pyrrolidinopropyl benzoate (I) and γ-pyrrolinopropyl benzoate (II) have been prepared and tested pharmacologically. It was thought that the latter compound would be particularly interesting as it would indicate the relative merits of an unsaturated structure in the production of local anesthesia.



I



II

These compounds were prepared by the condensation of γ-chloropropyl benzoate with the secondary amines, pyrrolidine and pyrroline, both of which were obtained by the reduction of pyrrole. Pyrrolidine was prepared by the catalytic reduction of pyrrole with Adams' platinum-oxide platinum black catalyst and pyrroline by the procedure of Knorr and Rabe,[3] which utilized zinc and hydrochloric acid as the reducing agent.

All attempts to reduce catalytically methyl and carbethoxy substituted pyrroles to the corresponding pyrrolidines were unsuccessful. While a small amount of reduction took place initially, the catalyst was soon poisoned and the reduction stopped. The catalyst could not be reactivated to any appreciable extent by shaking with oxygen. McCay and Schmidt[4] have reported a similar unsuccessful attempt to reduce the amide of pyr-

---

[1] This paper is taken from the thesis submitted by Leslie H. Andrews to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Arts.

[2] McElvain, THIS JOURNAL, 49, 2835 (1927).

[3] Knorr and Rabe, Ber., 34, 3491 (1901).

[4] McCay and Schmidt, THIS JOURNAL, 48, 1933 (1926).

role-carboxylic acid. On account of the negative results obtained in these experiments, the work on the preparation of the substituted pyrrolidinoalkyl benzoates was abandoned for the present.

Pyrrolidine condensed very smoothly with γ-chloropropyl benzoate and the resulting γ-pyrrolidinopropyl benzoate was isolated as the hydrochloride, which melted at 125–126°. In the case of the pyrrolino compound, however, considerable difficulty was experienced in obtaining a pure hydrochloride. It was quite difficult to separate and crystallize this hydrochloride from a reddish oil that accompanied it. It was finally purified and found to melt at 136–138°.

Experimental

Pyrrole.—This compound was prepared by a procedure developed by Katherine Bolliger[5] which is as follows. In a twelve-inch evaporating dish 630 g. (3 moles) of mucic acid was treated with an excess of ammonium hydroxide (about 900 cc., sp. gr. 0.9) and quickly stirred to a smooth paste. It was then evaporated to dryness on a steam cone. The ammonium mucate thus formed was powdered, treated with 250–400 cc. of glycerol, allowed to stand for several hours and then distilled from a 5-liter flask. Distillation was continued until no more oily drops came over. At this point the residue in the flask foamed considerably. The upper layer of the distillate was separated in a separatory funnel and steam distilled until all of the oily, insoluble liquid had passed over. The distillate was washed with water, dried over solid sodium hydroxide and redistilled. It boiled at 128–132° The yield varied from 80-100 g. (40–50%).

The pyrrole so obtained could not be reduced catalytically, but when it was distilled from over sodium in an atmosphere of hydrogen according to the procedure of Willstatter and Hatt,[6] a water-white product with an odor suggestive of chloroform was obtained. There was hardly any loss of pyrrole in this distillation from sodium and the product so obtained yielded to catalytic reduction.

Methylpyrroles.—The α- and β-methylpyrroles were prepared by a modification of the procedure of Oddo and Mameli.[7] To 17 g. (0.7 mole) of magnesium turnings and 200 cc. of dry ether, a solution of 76 g (0.7 mole) of ethyl bromide in 100 cc. of ether was added After the Grignard reagent had formed, a solution of 33.5 g. (0.5 mole) of pyrrole in 100 cc. of ether was added slowly and with constant stirring. The reaction was quite vigorous and had to be carefully regulated. After all of the pyrrole solution had been added the mixture was refluxed for thirty minutes and then a solution of 63 g. (0.5 mole) of dimethyl sulfate in 100 cc. of ether was slowly added. The mixture was then refluxed for one hour, after which it was cooled by an ice and salt mixture. Cold water was then added with stirring until the white salt which formed was completely dissolved. The water and ether layers were separated and the aqueous layer was extracted with an equal volume of ether. The ether was distilled off from the combined ether extracts and the residue steam distilled The pyrrole layer was separated from the water and the latter extracted with ether. The ethereal extract and the pyrrole layer were mixed and the resulting solution dried with anhydrous sodium sulfate, after which the ether was removed by distillation and the basic residue fractionated There were obtained 13 g. of unchanged pyrrole (b. p 125–132°) and 19.5 g. of a fraction that boiled at 132–155°, which consisted of a mixture of α- and β-methylpyrrole This

---

[5] Katherine Bolliger, University of Wisconsin "Thesis," 1926.

[6] Willstätter and Hatt, *Ber.*, 45, 1471 (1912).

[7] Oddo and Mameli, *Gazz. chim. ital.*, 43, 504 (1913).

fraction was distilled twice over sodium in an atmosphere of hydrogen before **it was** further used.

α-Carbethoxypyrrole.—This ester was prepared by the procedure of Oddo[8] from pyrryl magnesium bromide and ethyl chlorocarbonate. Although Oddo reported yields of 85–90% of this ester, it was not possible to obtain over 20% yields of the ester that boiled at 130–138° (20 mm.) in this work. On cooling the ester solidified and the solid ester melted at 36–38°.

Pyrrolidine.—A solution of 18 g. of pyrrole (which had been twice distilled from sodium) in 60 cc. of glacial acetic was shaken with hydrogen in the presence of 0.5 g. of Adams' platinum-oxide platinum black catalyst. The absorption of hydrogen was at all times quite slow and would periodically stop, but by shaking the reduction mixture with oxygen the catalyst could be reactivated and the reduction caused to proceed. After forty-five hours an additional 0.3 g. of catalyst was added. After 96–100 hours of shaking the theoretical amount of hydrogen had been absorbed. The platinum was allowed to settle and the dark-colored solution decanted. The acid was neutralized under a reflux with a concentrated solution of sodium hydroxide and then an excess of the alkali added. The alkaline solution was then steam distilled until the distillate no longer gave an acid reaction to litmus paper. The distillate (about 1 liter) was acidified with hydrochloric acid and evaporated to dryness on a steam cone. A dark red, gummy residue remained. This residue was treated with 40% sodium hydroxide and extracted with ether. The ether solution was dried with anhydrous sodium sulfate and then distilled. There was obtained 12 g. of pyrrolidine (63% of the theoretical) boiling at 85–88°. A crystalline hydrochloride of pyrrolidine could not be obtained.

Willstatter and Hatt[6] reduced pyrrole catalytically in glacial acetic acid solution and stated that the solution became deeply colored during the reduction. Hess[9] described the reduction of pyrrole under similar conditions stating that the coloration was coexistent with inhibitory effect and was careful to exclude oxygen from the catalyst, in which cases there was no coloration of the solution. Later, Willstatter and Waldschmidt[10] found that frequent shaking of the catalyst with oxygen is absolutely essential in the reduction of pyrrole. With this latter finding the results of the present work are in agreement, for it was only by frequent shaking with oxygen that the reduction could be caused to proceed.

Pyrroline (Dihydropyrrole).—Ciamician and Dennstedt[11] report the reduction of pyrrole to pyrroline using zinc and acetic acid as the reducing agent. Knorr and Rabe[3] report a similar reduction of pyrrole with zinc and hydrochloric acid at a temperature sufficiently low to prevent the resinification of the pyrrole by the strong mineral acid. Both procedures were tried in this work and it was found that the procedure of Knorr and Rabe gave the better results. Ciamician and Dennstedt report yields of 20% of the theoretical by their method, but it has been possible in this work to obtain 56% yields of pyrroline using a modified Knorr and Rabe procedure, which is as follows.

[8] Oddo, *Gazz. chim. ital.*, 39, I, 649 (1909); *ibid.*, **42,** II, 244 (1912).

[9] Hess, Ber., **46,** 3120 (1913).

[10] Willstätter and Waldschmidt, *ibid.*, 54, 113 (1921).

[11] Ciamician and Dennstedt, *ibid.*, 15, 1831 (1882); *ibid*, **16,** 1536 (1883).

Five hundred cc. of 20% hydrochloric acid is placed in a flask fitted with a mechanical stirrer, dropping funnel and a thermometer, cooled to 0° by means of an ice and salt mixture, and 200 g. of zinc dust is added with vigorous stirring. Fifty g. of pyrrole is then added slowly from a dropping funnel. It is important that the temperature of the liquid be kept low (0–10") at the start, else the speed of reaction will cause the temperature to get out of control. After all of the pyrrole had been added (about one hour), 300 cc. of concentrated hydrochloric acid was added and the stirring continued for two hours longer. The temperature was kept at 15–25° during this time The cooling bath was then removed and the mixture stirred for four and one-half hours at room temperature. The remaining zinc was then filtered off and washed with a little water The filtrate was made sufficiently alkaline to dissolve the precipitated zinc hydroxide and then steam distilled until the distillate was no longer alkaline to litmus. The distillate was made acid with hydrochloric acid and evaporated on a steam-bath. The remaining gummy residue was treated with an excess of 40% sodium hydroxide and extracted twice with ether. This ether extract was dried with anhydrous sodium sulfate and distilled. The pyrroline fraction boiled at 89–92° and weighed 28.5 *g*. There was also obtained 6.5 **g.** of a fraction that boiled at 115–125° (20 mm.). The hydrochloride of pyrroline was obtained crystalline and melted at 162–163°.

Attempted Reduction of **Methylpyrroles** and **α-Carbethoxypyrrole.**—A solution of 8 g. of the methylpyrrole fraction, twice distilled from sodium and boiling at 132–155°, was subjected to catalytic reduction as described above in the preparation of pyrrolidine. In the first twenty minutes there was a rapid absorption of hydrogen amounting to approximately one-eighth of the theoretical amount, but after this initial absorption of hydrogen the reduction stopped and could not be induced to continue either by shaking with oxygen or by the addition of fresh catalyst. Several runs were made with samples of platinum catalyst of known catalytic activity with similar results.

α-Carbethoxypyrrole in acetic acid solution gave practically the same results as the methylpyrroles on catalytic reduction. On account of the extremely small amount of hydrogen that was absorbed, no attempt to isolate a reduction product was made in either case.

γ-Pyrrolidinopropyl Benzoate Hydrochloride.—A mixture of 20 g. (2 moles) of pyrrolidine and 28 g. (1 mole) of γ-chloropropyl benzoate was heated on a steam-bath for one and one-half hours. The reaction mixture, which had separated into two layers, was then diluted with 100 cc. of ether and the oily, insoluble layer of pyrrolidine hydrochloride separated by carefully decanting off the ether solution. The ?-pyrrolidinopropyl benzoate was precipitated from the ether solution as the hydrochloride, which was recrystallized several times from an alcohol–ether mixture. The purified product weighed 14 g. and melted at 125–126°.

Anal. Calcd.: Cl, 13.15. Found: Cl, 13.25, 13.26.

γ-Pyrrolinopropyl Benzoate Hydrochloride.—A mixture of 10 g. (2 moles) of pyrroline and 14 g. (1 mole) of γ-chloropropyl benzoate was heated on a steam-bath for half an hour. The reaction mixture was worked up as described above in the preparation of y-pyrrolidinopropyl benzoate hydrochloride. The hydrochloride of the pyrrolino derivative so obtained was quite difficult to crystallize and was found by analysis to contain a higher percentage (15.05%) of halogen than its formula required, which fact indicated that some pyrroline hydrochloride was mixed with it. Accordingly it was found advisable to shake the crude pyrrolinopropyl benzoate hydrochloride with 10% sodium hydroxide and benzoyl chloride. After this procedure the tertiary amine was reprecipitated from ether as the hydrochloride, which was recrystallized twice from an alcohol-ether mixture and twice from acetone. The product so obtained weighed **3.5** g. and melted at 136–138°.

Anal. Calcd.: 13.25. Found: Cl, 13.58, 13.58

The melting point of a mixture of the pyrrolidino and pyrrolino derivatives was depressed to 75° and it was completely molten at 120°. The latter compound when shaken with dilute potassium permanganate solution caused immediate decolorization, while the former reacted very slowly with this reagent.

Pharmacological Report

γ-Pyrrolidinopropyl benzoate hydrochloride (I) and γ-pyrrolinopropyl benzoate hydrochloride (II) are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Indianapolis, Indiana. A preliminary report of this work, given in the table below, includes subcutaneous and intravenous toxicity determinations and measurements of the duration of anesthesia produced by the application of a 2% solution of the anesthetic to the rabbit's cornea. The corresponding values for γ-piperidinopropyl benzoate hydrochloride (III), cocaine and procaine taken from another paper[12] are included for comparison,

TABLE I

PHARMACOLOGICAL DATA

Compound	Av. dur. of anesthesia, min.	Subcutaneous toxicity to white mice (mg./kg.) M. T. D.	M. L. D.	No. of mice used	Intravenous toxicity to white rats (mg./kg.) M. T. D.	M. L. D.	No. of rats used
I	15	400	450	9	17.5	20	9
II	5	1000	1100	11	25	30	8
III	0	400	450	8	15	17.5	10
Cocaine	29	200	250	18	15	17.5	12
Procaine	0	900	1000	17	45	50	10

Discussion of Pharmacological Data

It is seen that the pyrrolidinopropyl benzoate (I) is a much more efficient anesthetic than the compound (III) that contains the piperidine nucleus instead of the pyrrolidine nucleus. This, it seems, would not have been expected, for practically all of the data which are available on the physiological behavior of various types of local anesthetic indicate that in a particular series[13] of compounds the substances of higher carbon content are more active physiologically (considering either toxicity or production of anesthesia or both) than those of lower carbon content. Compounds I and III have very similar structures, the only difference being that III contains one CH_2 grouping more in its cyclic structure than I. The effect of the double bond in II is quite marked, for when compared with I it is seen that

---

[12] McElvain, THIS JOURNAL, 49, 2839 (1927).

[13] For example, in the dialkylamino-alkyl-*p*-aminobenzoate series, an increase in size of the alkyl groups attached to the nitrogen atom causes an increase in both toxicity and anesthetic action [Schmitz and Loevenhart, *J. Pharm. Exptl. Ther.*, 24, 159 (1924)], and in the 1-alkyl-3-carbethoxy-4-piperidyl benzoates and *p*-aminobenzoates an increase in the size of the alkyl group causes an increased anesthetic action with a decreased toxicity [McElvain, THIS JOURNAL, 48, 2179, 2239 (1926)].

this change in structure causes a very great lowering in the physiological activity of the compound.

Summary

1. It has been found that while pyrrole can be reduced catalytically to the tetrahydro derivative, the methyl and carbethoxy substituted pyrroles could not be similarly reduced.

2. γ-Pyrrolidinopropyl benzoate and γ-pyrrolinopropyl benzoate have been prepared and tested pharmacologically as local anesthetics. It was found that the presence of the double bond in the latter greatly reduces its anesthetic activity. The pyrrolidino derivative was shown to have greater anesthetic action than the corresponding piperidino derivative. It is pointed out that this was an unexpected relationship, since data on other series of anesthetics indicated that the reverse should be true.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

SOME DERIVATIVES OF TRIMETHYLETHYLSTANNANE

BY RALPH H. BULLARD AND RAYMOND A. VINGEE

RECEIVED OCTOBER 30, 1928 PUBLISHED MARCH 6, 1929

The study of the organic compounds of tin has been continued by investigating certain derivatives of trimethylethylstannane, $(CH_3)_3C_2H_5Sn$.

The hydride, dimethylethylstannane, $(CH_3)_2C_2H_5SnH$, derived from trimethylethylstannane by the substitution of a hydrogen atom for a methyl group, is of particular interest. It is oxidized by the air, being converted into the corresponding hydroxide. The reaction is represented by the equation $2(CH_3)_2C_2H_5SnH + O_2 = 2(CH_3)_2C_2H_5SnOH$. This oxidation is interesting in view of the fact that trimethylstannane, $(CH_3)_3SnH$, prepared by Kraus and Greer[1] is stable in the air, whereas triphenylstannane, $(C_6H_5)_3SnH$, prepared by Chambers and Scherer[2] oxidizes in the air to hexaphenylstanno-ethane, $(C_6H_5)_3SnSn(C_6H_5)_3$, with the formation of water.

Trimethylethylstannane, $(CH_3)_3C_2H_5Sn$.—This compound has been prepared by Cahours[3] from trimethylstannyl iodide and zinc diethyl, and also by Pope and Peachey[4] by the use of the Grignard reaction. The following method may also be used to advantage.

Trimethylstannyl bromide, $(CH_3)_3SnBr$, was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of bromide. On adding ethyl bromide slowly the yellow color of the

---

[1] Kraus and Greer, THIS JOURNAL, 44, 2629 (1922).

[2] Chambers and Scherer, *ibid.*, 48, 1054 (1926).

[3] Cahours, Ann., 122, 48 (1862).

[4] Pope and Peachey, *Proc. Chem. Soc.*, 19, 290 (1903).

sodium salt was discharged and trimethylethylstannane was precipitated. The reaction took place as follows: $(CH_3)_3SnNa + C_2H_5Br = (CH_3)_3C_2H_5Sn + NaBr$. The ammonia was allowed to evaporate and water was added. The lower layer of colorless oil was separated, dried over anhydrous calcium chloride and distilled. That portion boiling at 107–108° was collected as the pure stannane; yield, 80%.

Mol. wt. Subs., 0.4158, 0.6448: C_6H_6, 21.30, 21.30; Δt, 0.515, 0.784. Calcd. for $(CH_3)_3C_2H_5Sn$: mol. wt., 192.7. Found: 189.5, 193.1; av. 101.3.

Anal. Subs., 0.3830, 0.5569: SnO_2, 0.2096, 0.4374. Calcd. for $(CH_3)_3C_2H_5Sn$: Sn, 61.60. Found: 61.61, 61.86.

Bromination of Trimethylethylstannane.—The stannane was cooled in running water and the calculated amount of a carbon tetrachloride solution of bromine was slowly added. Bromination took place readily. The reaction mixture was fractionally distilled and the portion coming over at 175–180° was collected.

Anal. Subs., 0.4890, 0.2321, 0.1091: AgBr, 0.3621, 0.1682, 0.0792. Calcd. for $(CH_3)_2C_2H_5SnBr$: Br, 31.02. Found: 31.51, 30.84, 30.85.

Ammonia gas was passed into a carbon tetrachloride solution of dimethylethylstannyl bromide. A white precipitate of the ammonia complex was obtained. This complex salt was not stable, for on standing it softened and the odor of the bromide became evident.

Dimethylethylstannane, $(CH_3)_2C_2H_5SnH$.—Dimethylethylstannyl bromide was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of bromide. Excess ammonium bromide was then slowly added. The reaction proceeded as follows: $NaSnC_2H_5(CH_3)_2 + NH_4Br = (CH_3)_2C_2H_5SnH + NaBr + NH_3$. When the reaction was completed, the reaction tube was connected to a receiver immersed in liquid ammonia and the ammonia in the reaction tube was allowed to evaporate. The reaction tube was then warmed in a water-bath at 100° while a slow stream of ammonia gas was passed through the tube. The stannane was thus vapor-distilled from the reaction tube into the cooled receiver. The stannane boils at 90° under atmospheric pressure.

Anal. Subs., 0.4930: SnO_2, 0.4135 Calcd. for $(CH_3)_2C_2H_5SnH$: Sn, 66.42. Found: Sn, 66.07.

Mol. *wt.* Subs., 0.1290, 0.0843: 387 cc. (33.5 and 24.5 mm. at 22°). Calcd. for $(CH_3)_2C_2H_5SnH$: mol. wt., 178.7. Found: 182.9, 177.3; av., 180.1.

Oxidation of Dimethylethylstannane.—In order to preserve the stannane in the pure state it was found necessary to keep it sealed in tubes under nitrogen. The capillary at the end of the tube containing some dimethylethylstannane was broken, thus allowing the air to enter. After a few days the tube contained a mass of white, needle-like crystals which were found to be very hygroscopic.

Anal. Subs,, 0.0883, 0.1382: SnO_2, 0.0681, 0.1072 Calcd. for $(CH_3)_2C_2H_5SnOH$: Sn, 60.96. Found: Sn, 60.75, 61.10.

Dimethylethylstannyl hydroxide was also prepared from dimethylethylstannyl bromide by treating the bromide with 30% sodium hydroxide solution. The reaction mass was extracted with ether, the ether solution dried over anhydrous calcium chloride and the ether removed by boiling under reduced pressure at room temperature. There remained a mass of white crystals which, too, were hygroscopic.

Anal. Subs., 0.2492: SnO_2, 0.1926. Calcd. for $(CH_3)_2C_2H_5SnOH$: Sn, 60.96. Found: Sn, 60.88.

The authors wish to acknowledge their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of the present investigation.

Summary

1. Trimethylethylstannane has been prepared in yields of 80% by treating sodium trimethyl stannide with ethyl bromide.

2. On brominating trimethylethylstannane a methyl group is removed and dimethylethylstannyl bromide is formed.

3. Dimethylethylstannane has been prepared by treating sodium dimethyl ethyl stannide in liquid ammonia with ammonium bromide.

4. On slow atmospheric oxidation of dimethylethylstannane there is formed dimethylethylstannyl hydroxide.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

THE ACTION OF BASES ON CERTAIN MERCURATED ANILINES

BY FRANK C. WHITMORE, E. R. HANSON AND F. L. CARNAHAN[1]

RECEIVED NOVEMBER 2, 1928 PUBLISHED MARCH 6, 1929

A reaction which has received considerable study in this Laboratory is the conversion of mercury compounds of the type RHgX into the so-called "mercuri-bis" compounds of the type R_2Hg, in which both valences of the mercury are attached to carbon.

$$2\,RHgX \rightleftharpoons R_2Hg + HgX_2$$

This reaction readily goes to the left without any special precautions. It can be made to go to the right by a great variety of reagents, such as iodides, sulfides, thiosulfates, cyanides, sodium stannite and metals such as copper and sodium. For some time the working hypothesis in this Laboratory was that the formation of the mercuri-*bis* compounds could be brought about by "any reagent which removes mercuric ions more completely than does sodium hydroxide." This hypothesis proved useful but

---

[1] This work was carried on during the years 1923–1927 under grants from the Public Health Institute of Chicago.

was apparently contradicted by an observation of Pesci[2] that 3-acetoxymercuridimethyl-*p*-toluidine on standing with aqueous ammonia gives the corresponding mercuri-bis compound. After unsuccessful attempts to repeat this work, it was decided to use a more drastic treatment with potassium hydroxide. Indications early were found that certain mercurated dialkylanilines when treated with aqueous alcoholic potassium hydroxide gave traces of the mercuri-bis compounds. Great difficulty was found in applying this generally, however, even in this series. By the use of more concentrated solutions it has been possible to show that the reaction is general for the p-mercurated dialkylanilines. The *p*-acetoxymercuri compounds of dimethylaniline, diethylaniline, di-*n*-propylaniline, di-*n*-butylaniline, methylethylaniline and benzylethylaniline on refluxing with concentrated aqueous alcoholic solutions of potassium hydroxide give the corresponding mercuri-bis compounds.

The general method used in forming the mercuri-bis compound was to reflux for thirty minutes one mole of the mercurated aniline with 32 moles of potassium hydroxide in a solution of **100** moles of alcohol and **100** moles of water. In the case of p-acetoxymercuridiethylaniline only a trace of the mercuri-bis compound was obtained under these conditions. The use of 64 moles of potassium hydroxide gave the desired substance in small quantities.

The yields of the mercuri-*bis* compounds were small under the conditions of the experiments. Quantities large enough for separation and identification were all that were desired. It is no doubt possible to increase the yield greatly by proper variation of the conditions and concentrations.

The chief products accompanying the mercuri-his compounds were organomercuri oxides and hydroxides. The inorganic mercury produced as a result of the formation of mercuri-bis compounds appeared largely as mercurous and mercuric oxides. In the case of *p*-acetoxymercuridimethylaniline the formation of metallic mercury took place. The amount of insoluble material removed by hot filtration of the various reaction mixtures is consistent with the quantity of mercuri-his compound formed. The formation of ethane-hexamercarbide is also possible under the conditions. Mercuric oxide reacts with alcoholic alkali to form this substance. In the case of the action of p-acetoxymercuridimethylaniline with 32 moles of potassium hydroxide, the formation of a small amount of the mercarbide was proved.

The formation of the mercuri-bis compounds by means of aqueous alcoholic potassium hydroxide in the case of mercury compounds containing the $-NR_2$ group is probably very complex in mechanism. Undoubtedly the result is due chiefly to the existence of an alkaline reducing environment due both to the alkylated amines and the potassium ethylate present.

---

[2] Pesci, *Gazz. chim. ital.*, **28**, II, 106 **(1898)**.

The various steps in the reactions may be indicated as follows

$$RHgOCOCH_3 \longrightarrow RHgOH \rightleftharpoons (RHg)_2O \rightleftharpoons R_2Hg + HgO$$

The mercuric oxide is partly reduced to mercurous oxide or mercury and partly converted to the very insoluble ethane-hexamercarbide.

Experimental Part

Crystalline **p-Bromomercuri-aniline,** $BrHgC_6H_4NH_2$.—Five g. of *p*-acetoxymercuri-aniline was refluxed with a solution of 2 g. of sodium bromide in 1500 cc. of water for three hours. A small amount of undissolved material was removed by filtration. On cooling the filtrate deposited colorless, lustrous plates. When dried in air these became slightly greenish; yield, 1.8 g.; m. p. 181°.

Anal. Subs., 0.2112, 0.2206: Hg, 0.1147, 0.1202. Calcd. for C_6H_6NBrHg: Hg, 53.9. Found: Hg, 54.3, 54.4.

Crystalline **p-Iodomercuri-aniline,** $IHgC_6H_4NH_2$.—This substance was prepared similarly to the bromomercuri compound. The fine, flat plates which separated from the hot filtrate were crystallized from 250 cc. of hot alcohol. On drying the crystals assumed a slightly golden tint; yield, 1.2 g.; m. p. 165°.

Anal. Subs., 0.2023: Hg, 0.0971. Calcd. for C_6H_6NIHg: Hg, 47.8. Pound: Hg, 47.9.

Treatment of *p*-Acetoxymercuri-aniline with Potassium Hydroxide.—To a solution of 44.8 g. of potassium hydroxide in 35 cc. of water and 153 cc. of 95% alcohol was added 8.79 g. of *p*-acetoxymercuri-aniline (mercury compound 1 mole, potassium hydroxide 32 moles, alcohol 100 moles, water 100 moles). The mixture was refluxed for thirty minutes. A yellow precipitate was formed during the reaction. This was filtered off, washed with cold water and air dried. Its insolubility in alcohol, ether, chloroform, benzene and acetone, together with the fact that it decomposed on heating, proved that it was not the mercuri-*bis* compound. This is probably the usual compound formed by the action of concentrated alkalies on p-acetoxymercuri-aniline. Its true formula apparently is not known.

p-Acetoxymercuri-di-alkyl-anilines, $R_2NC_6H_4HgOCOCH_3$.—These substances were prepared by mercurating the N-di-substituted anilines with mercuric acetate in a mixture of water, 95% ethyl alcohol and acetic acid. With the last two the reaction mixtures gave no crystals until most of the acid had been neutralized by sodium hydroxide.

TABLE I

ANALYTICAL AND OTHER DATA

R_2	M. p., °C.	Yield, %	Hg, calcd.	Hg, found[a]
Dimethyl	165	82	..	..
Diethyl	105	51	..	..
Di-*n*-propyl	99	90	46.1	45.9
Di-*n*-butyl	89–90	91	43.3	43.4
Methylethyl	92–93	85	51.0	51.0
Benzylethyl	92–94	72	42.7	42.8

[a] Mercury analyses were made by the "gold crucible" method.

p-Halogenmercuri Compounds.—The ClHg- and BrHg-compounds were made by refluxing alcoholic solutions of the acetoxymercuri compound with calcium chloride and sodium bromide, respectively. The IHg-compounds were made by means of exactly equivalent amounts of sodium iodide in cold acetone.

TABLE II

ANALYSES

R	ClHg-compounds M. p., °C.	Mercury, %		BrHg-compounds M. p., °C.	Mercury, %		IHg-compounds M. p., °C.	Mercury, %	
		Calcd.	Found.		Calcd.	Found		Calcd.	Found
Diethyl	.....	..	..	158	46.8	46.1"	120–121	42.2	41.9"
Di-*n*-propyl	170–172	48.7	48 7	16.5167	43.9	43.8	150	39.8	39.7[a]
Di-n-butyl	162–163	45.5	45.0"	164–165	41.4	41.1"	151	37.7	37.3"
Methylethyl	162–166	54.2	53.2[a]	154–155	48.4	48.2	137–138	43.5	43.3
Benzylethyl	150–151	45.0	44.7	155	40.9	41.2	132–134	37.3	37.3

[a] Average of two or more analyses.

Action of the Acetoxymercuri Compounds with Alcoholic Potassium Hydroxide.—In each case the acetoxymercuri compound was boiled for thirty minutes with the indicated molecular proportions of potassium hydroxide, 100 moles of ethyl alcohol and 100 moles of water.

TABLE III

ANALYTICAL AND OTHER DATA

R	Hg cpd. g.	Mole ratio Hg cpd.	Mole ratio KOH	Product	M. p., °C.	Mercury, % Calcd.	Mercury, % Found
Dimethyl	9.5	1	1	$(CH_3)_2NC_6H_4HgOH$[a]	152–156	59.4	59.3[b]
	9.5	1	1	$((CH_3)_2NC_6H_4Hg)_2O$[c] and	180	61.1	61.2[b]
				hydroxide	153–156	59.4	59.3[b]
	9.5	1	2	Oxide	180	61.1	60.8[b]
	9.5	1	4	Oxide	180	61.1	61.1[b]
	9.5	1	8	$((CH_3)_2NC_6H_4)_2Hg$[d]	168	45.3	45.4[b]
				and oxide	180	61.1	60.7
	9.5	1	16	Hg-*bis* compound	168	45.3	45.6
				and oxide	180	61.1	60.7
	9.5	1	32	Hg metal and oxides, Hg-bis	168	45.3	45.5
				compound and oxide	180	61.1	61.0[b]
Diethyl	10 2	1	32	$((C_2H_5)_2NC_6H_4)_2Hg$ (trace)			
				and $((C_2H_5)_2NC_6H_4Hg)_2O$	210–219	56.2	56.4
	10.1	1	64[d]	Oxide and Hg-bis compound[e]	161	40.4	40.4
Di-n-propyl	10.9	1	32	$((C_3H_7)_2NC_6H_4)_2Hg$[f]	86	36.3	36.5
				$((C_3H_7)_2NC_6H_4Hg)_2O$	184–185	52.2	52.3[b]
Di-*n*-butyl	11.6	1	32	$((C_4H_9)_2NC_6H_4)_2Hg$[g]	79–80	33.0	33.2
				$((C_4H_9)_2NC_6H_4Hg)_2O$	170	48.6	48.7[b]
Methylethyl	9.8	1	32	$(CH_3)(C_2H_5)NC_6H_4)_2Hg$[h]	139–142	42.8	42.0
				$(CH_3)(C_2H_5)NC_6H_4HgOH$	192–199	57.0	56.4[b]
Benzylethyl	11.7	1	32	$((C_6H_5CH_2)(C_2H_5)NC_6H_4)_2Hg$[i]	128	32.3	32.5
				$(C_6H_5CH_2)(C_2H_5)NC_6H_4Hg$- OH	158–167	46.9	46.6[b]

[a] Boiled for only ten minutes.

[b] Average of two or more analyses.

[c] Boiled for twenty minutes.

[d] The fact that this product was *p*-mercuri-*bis*-dimethylaniline was confirmed by

refluxing it with mercuric chloride in alcohol. The theoretical yield of *p*-chloromercuridimethylaniline was obtained; m. p., 225°; Hg calcd., 56.3; found, 56.2. Sodium hydroxide under similar conditions gave the same products.

[e] Treatment with mercuric chloride gave the chloromercuri compound; m. p., 164°; Hg calcd., 52.2; found, 51.8.

[f] Mercuric chloride gave the ClHg-compound; m. p., 171°; Hg calcd., 48.7; found, 48.5.

[g] The ClHg-compound was prepared as usual; m. p., 162–163°; Hg calcd., 45.6; found, 45.8.

[h] ClHg-compound, m. p., 165°; Hg calcd., 54.2; found, 53.0.

[i] ClHg-compound, m. p., 150–151°; Hg calcd., 45.0; found, 44.0.

Action of Sodium Ethylate on *p*-Acetoxymercuridiethylaniline.—(a) Four g. of sodium was dissolved in 54 g. of absolute alcohol. To the solution of sodium ethylate thus formed was added a solution of 2 g. of p-acetoxymercuridiethylaniline in 8 g. of absolute alcohol. The mixture was refluxed for twenty minutes. Metallic mercury separated from the reaction mixture. No mercuri-bis compound was obtained.

(b) Eight g. of sodium was dissolved in 94 g. of absolute alcohol and to the solution of sodium ethylate thus formed was added a solution of 2 g. of *p*-acetoxymercuridiethylaniline in 8 g. of absolute alcohol. The mixture was refluxed for twenty minutes. No mercuri-bis compound was detected in the reaction products.

(c) More vigorous treatment with sodium ethylate gave completely unmanageable products.

Preparation of Mercuri-*bis* Compounds from Acetoxymercuri Compounds and Sodium Iodide.—The reactions were carried out in cold acetone solution using an excess of the iodide.

TABLE IV

ANALYTICAL AND OTHER DATA

	Hg-*bis* compound		Mercury, %		
R	Yield. %	M. p., °C.	Calcd.	Found	
Dimethyl	40	168–169[a]	..	..	..
Diethyl	31	160–161"	..	..	..
Di-*n*-propyl	39	86[a,b]	36.3	36.5	36.4
Di-*n*-butyl	50	80– 81	..	..	..
Methylethyl	..	133–135[c]	42 8	42.3	42.5
Benzylethyl	..	125–126[d]	32.2	32.6	32.6

[a] The melting point was not lowered by mixing with the Hg-*bis* compound obtained by means of alcoholic potassium hydroxide.

[b] The Hg-*bis* compound was further identified by conversion to the ClHg-compound, m. p. 170°.

[c] It was converted to the ClHg-compound, m. p. 161–165°. A 1:1 mixture of the Hg-*bis* and IHg-compounds melted at 100–122°.

[d] The ClHg-compound was obtained from it, m. p. 149–150°. A mixture of the Hg-*bis* and IHg-compounds melted at 110–120°.

Conversion of the Acetoxymercuri Compounds to the Mercuri–bis Compounds by Sodium **Thiosulfate** in cold concentrated aqueous solution.

TABLE V

MERCURI-*bis* COMPOUNDS

R	*Kg-his* compound Yield, %	M. p., °C.	Mercury, % Calcd.	Pound	
Di-n-propyl	**38**	**86**	..	..	..
Di-n-butyl	..	**80– 81**	**33.0**	**31.8**	**32.3**
Methylethyl"	..	132–133[b]	..	..	..
Benzylethyl[a]	**28**	125[b]	..	..	..

[a] The Hg-*bis* compound could not be obtained from the acetoxymercuri compound but was produced in small amount by treating an alcohol suspension of the hydroxymercuri compound with concd. aqueous sodium thiosulfate.

[b] The m. p. was not lowered by addition of known Hg-*bis* compound.

Formation of **Ethane-hexamercarbide.**—(a) A mixture of 7.96 g. of mercuric acetate, 44.8 g. of potassium hydroxide, 35 cc. of water and 153 cc. of alcohol (mercuric acetate 1 mole, potassium hydroxide 32 moles, water 100 moles, alcohol 100 moles) was refluxed for thirty minutes. The residue on hot filtration was washed with water and dilute alkali. It was then digested with 20% nitric acid until it became white. The solid was filtered off, washed with water and digested with potassium hydroxide solution. The residue was filtered, washed with water and air dried. The product was yellowish; yield, 0.64 g. It exploded violently at 230".

(b) p-Acetoxymercuridimethylaniline was treated with 32 moles of potassium hydroxide as above using four times the quantities listed. The residue from hot filtration was treated like that obtained in (a). Ethane-hexamercarbide was separated in a yield of 0.25 g. It exploded violently at 230°.

The formation of ethane-hexamercarbide is no doubt a secondary reaction. Mercuric oxide is set free by the formation of the mercuri-his compound. This reacts with alcohol in the presence of alkali to form ethane-hexamercarbide. No attempt to isolate the substance from other reactions in which mercuri-his compounds were formed was made. The conditions necessary for its formation, however, were satisfied in all cases.

Summary

1. Mercuri-bis compounds of the type R_2Hg have been obtained from six mercurated dialkylanilines by reaction with alcoholic potassium hydroxide, a new reagent for producing this change.

2. Crystalline p-bromomercuri- and *p*-iodomercuri-aniline have been prepared for the first time.

3. Earlier work on mercury derivatives of diethylaniline has been confirmed and extended.

4. Series of mercury derivatives have been prepared from di-n-propyl-, di-n-butyl-, methylethyl- and benzylethylanilines.

5. The conversion $RHgX \longrightarrow R_2Hg$ has also been accomplished in all these cases by means of sodium iodide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY. NO. 594]

A STUDY OF SOME OF THE REACTIONS OF 3-HYDROXY-6-AMINOTOLUENE AND OF CERTAIN OF ITS DERIVATIVES[1,2]

BY MARSTON TAYLOR BOGERT AND GEORGE HERBERT CONNITT

RECEIVED NOVEMBER 5, 1928 PUBLISHED MARCH 6, 1929

Since this o-amino-m-cresol is an industrial by-product, it seemed desirable to investigate it somewhat more fully as a possible source of useful intermediate or final products.

Because of its p-aminophenol structure, the first line of attack consisted in the synthesis of derivatives analogous to various well-known synthetic drugs, but none of these products have been subjected as yet to pharmacological examination. It is hoped that, since m-cresol is a somewhat stronger antiseptic than phenol, and the toluidines are less toxic than aniline, there may be some advantages in these new products, although Heubner[3] and Rhode[4] have pointed out that the analogous derivatives of *o,o*-dimethyl-p-phenetidine are all inferior therapeutically to those of p-phenetidine itself.

The simple phenacetin homolog, 3-ethoxy-6-acetylaminotoluene, is somewhat more soluble in water than phenacetin. The most soluble derivative of this type prepared in the course of the work was the 3-hydroxyethoxy-6-acetylaminotoluene, which structurally resembles "Pertonal," a drug stated by Cow[5] to be far less toxic than phenacetin, and as antipyretic to possess a much feebler but longer continued action. Like salicylyl-p-phenetidide, the corresponding salicylylaminocresol derivative was too resistant to hydrolysis to hold out much promise as a medicament. "Malakin" is the trade name under which salicylal-p-phenetidine has been marketed. It is stated to be a good analgesic, but too difficultly soluble in water. We synthesized the aminocresol analog and the corre-

---

[1] Presented in abstract before the Organic Division, at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] This investigation was made possible through the generous assistance of the Verona Chemical Co., North Newark, N. J., who, through their Chief Chemist, Dr. Jacob Ehrlich, supplied us with the necessary raw material. We take this opportunity of expressing our thanks to both of them.—M. T. B.

[3] Heubner, *Biochem.* Z., **93**, 395 (1919).

[4] Rhode, *Ber.* deut. *pharm. Ges.*, 31,271 (1921).

[5] Cow, J. *Pharmacol.*, 12,343 (1919).

sponding hydroxy derivative, but they are likewise but very slightly soluble in water.

Bender[6] and also Chattaway and Orton[7] have shown that acetylated anilines, when treated with hypochlorous acid, give chloro-amino derivatives which are unstable when the positions ortho or para to the nitrogen are either of them unoccupied, and that heating, alone or in solution, causes the halogen to migrate from the nitrogen to the ring. In the case of 3-ethoxy-6-acetyl-aminotoluene, when we applied Bender's method of treatment with hypochlorite, the product was a stable dichloride which lost no halogen when hydrolyzed by concentrated hydrochloric acid and was identified as the 2,4-dichloro-3-ethoxy-6-acetylaminotoluene by ethylation of the 2,4-dichloro-3-hydroxy-6-acetylaminotoluene. Further, the saponification product gave a stable hydrochloride, which would scarcely have been the case if the halogen had been adjacent to the amino group.

Staedel and Kolb[8] have shown that the action of hypochlorous acid on aminocresol hydrochloride yields the toluquinonechlorimide, but we found that excess of hypochorous acid converted the acetylaminocresol into 2,4-dichlorotoluquinone-6-acetimide, the structure of which was proved by its oxidation to 2,4-dichlorotoluquinone and its reduction to the 2,4-dichloro-6-acetylaminocresol, the structures of both of which have been established by Raiford.[9]

The reason for this 2,4-disubstitution is apparently the orienting influence of both the methyl and hydroxy (or ethoxy) groups toward these positions while only the acetylamino group tends to direct the halogen to Position 5. The chlorination thus follows the same course as in m-cresol itself.

Nitration of 3-hydroxy-6-acetylaminotoluene gave the 2,4-dinitro derivative. With the 3-acetoxy-6-acetylaminotoluene, nitration yielded the 5-nitro-acetylamino acetate, unless the reaction was carried out in such a way that some hydrolysis of the acetoxy group occurred, in which event the 3-hydroxy-2,4-dinitro derivative was also formed.

In the case of the 3-ethoxy-6-acetylaminotoluene, nitration in glacial acetic acid solution resulted in a mixture of approximately 85–90% of the 4-nitro derivative with 10–15% of the 5-nitro isomer. That the isomer formed in larger amount was the 4-nitro derivative was proved by the formation of 3-ethoxy-4-nitrotoluene by elimination of the acetylamino group, as well as by its other properties.

For these 6-acetylaminotoluenes, then, the hydroxyl group in Position 3 directs the entering nitro groups to 2 and 4. When the hydroxyl is ethylated, the 4-nitro is the chief product, with only a small quantity of

---

[6] Bender, *Ber.*, 19, 2272 (1886).

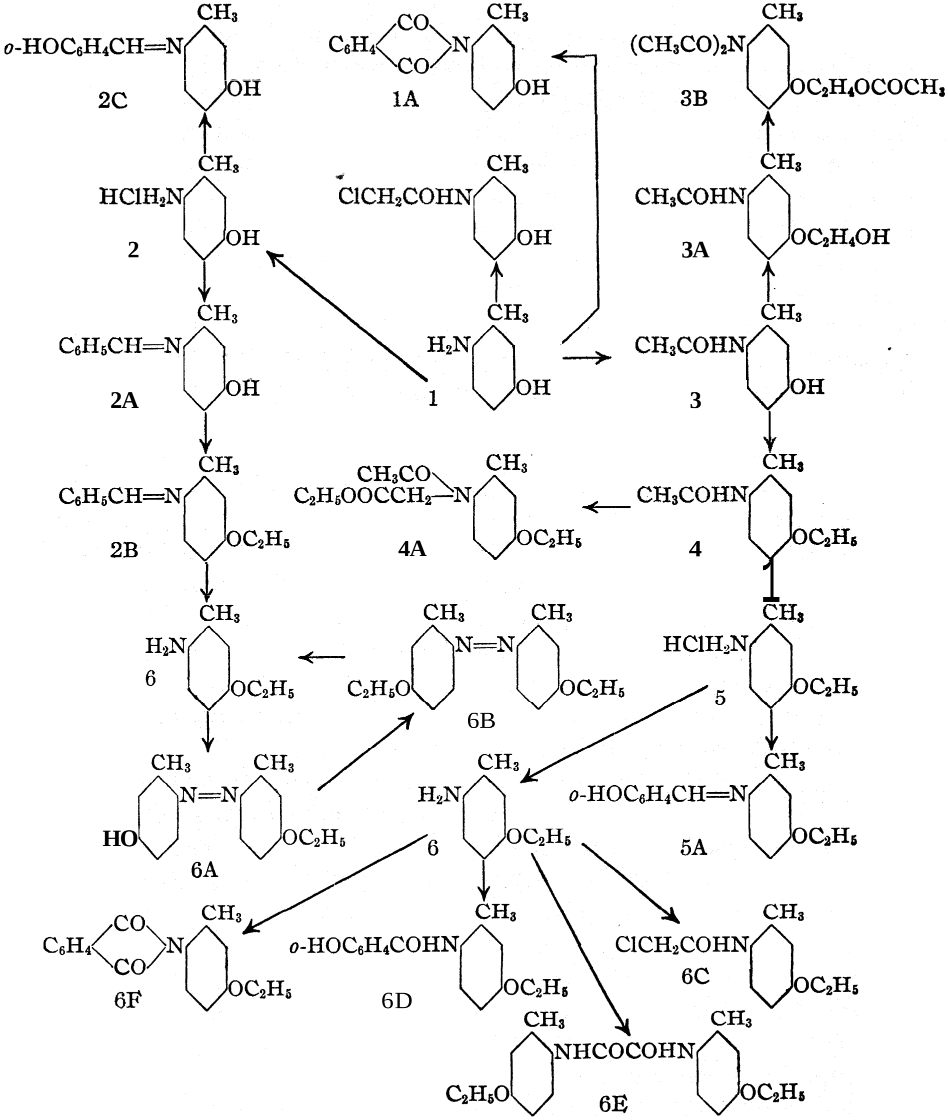
[7] Chattaway and Orton, *J. Chem. Soc.*, 75, 1046 (1899).

[8] Staedel and Kolb, *Ann.*, 259, 218 (1890).

[9] Raiford, *Am. Chem. J.*, 46, 417 (1911).

the 5-nitro isomer. But when the hydroxyl is acetylated, the nitro group enters Position 5 practically exclusively.

Nitration of 3-ethoxy-6-acetylaminotoluene with stronger acid, under the same conditions employed for the preparation of the 2,3-dinitro derivative from phenacetin,[10] gave similar results with the 3-ethoxy-6-acetylaminotoluene, the product being the 4,5-dinitro derivative.



Flow Sheet. General Products

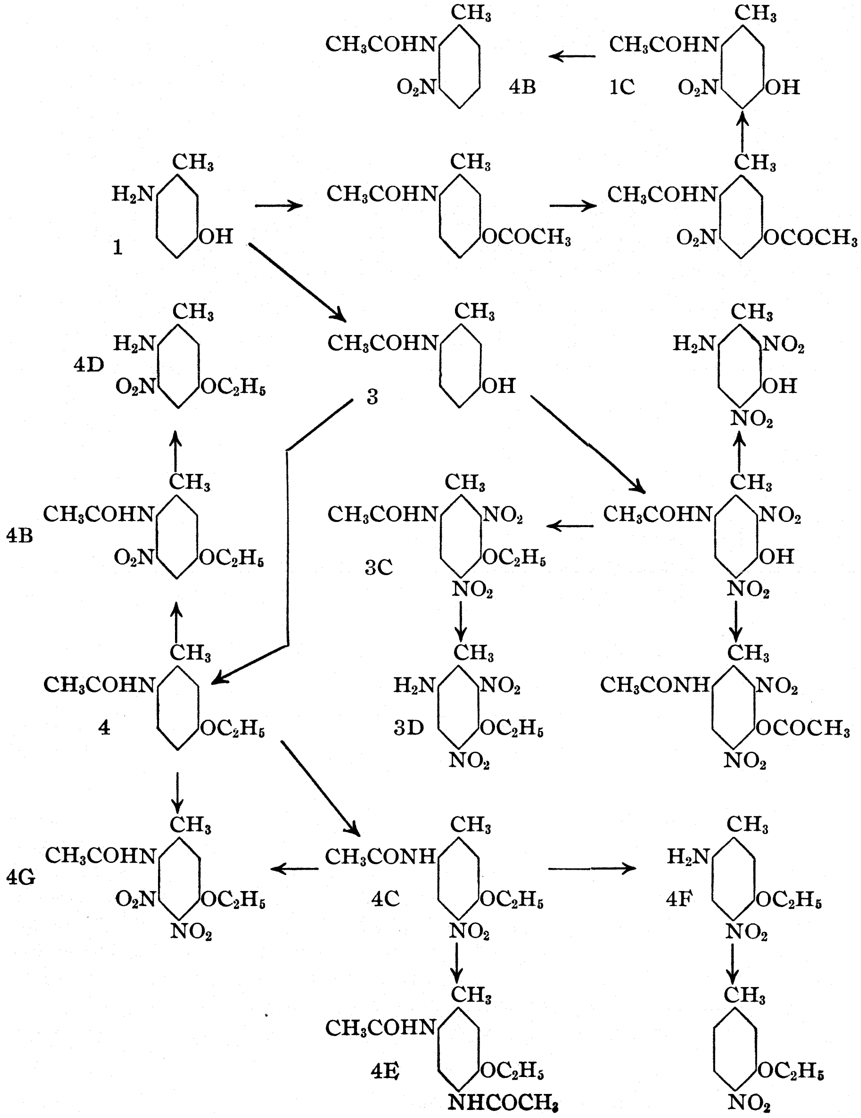
---

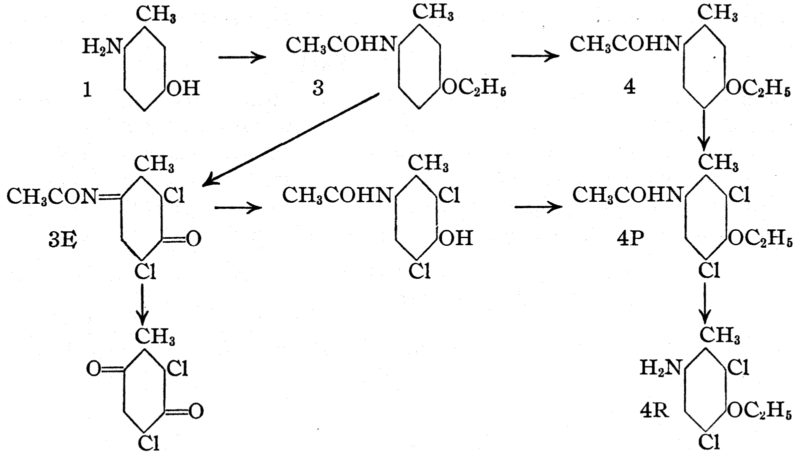
[10] Blanksma, *Rec. trav. chim.*, **27**, 49 (1908).

The synthetic work is presented diagrammatically in the Flow Sheets.

Experimental Part

3-Hydroxy-6-aminotoluene Hydrochloride.—After boiling the crude aminocresol (100 g.) with dilute hydrochloric acid (200 cc. of concentrated acid + 400 cc. of water) until dissolved, the solution was digested for an hour with Norite (40 g.) and filtered hot. As the clear red filtrate cooled, it deposited square, greenish plates whose color faded somewhat on drying. Recrystallized from dilute (1:2) hydrochloric acid, colorless plates were obtained, soluble in water or alcohol, which began darkening above





Flow Sheet. Substituted Products

250° and decomposed at about 290° (uncorr.); yield, about 80%. It was prepared first by Staedel and Kolb,[11] by the reduction of the nitrocresol with tin and hydrochloric acid.

This salt was used as our initial material, rather than the free base, because of its greater stability and the ease with which it could be obtained practically pure.

3-Hydroxy-6-benzalaminotoluene.—To a solution of the aminocresol hydrochloride (10 g.) in water (100 cc.), containing some sodium bisulfite (0.1 g.) to prevent oxidation, there was added an equimolar amount (6.62 g.) of benzaldehyde and slightly more (105%) than the calculated quantity of an aqueous solution of sodium acetate. The mixture was shaken vigorously and frequently during two hours. The pale, tan-colored flocculent precipitate of the crude benzal derivative was crystallized from benzene, alcohol or dilute acetic acid. From benzene it separated in needles, from the other solvents in blades, both forms melting at 135.5° (corr.); yield, practically that calculated.

Anal. Calcd. for $C_{14}H_{13}ON$: C, 79.60; H, 6.20. Found: C, 79.45; H, 6.02.

It proved to be easier to get a pure benzal derivative from the hydrochloride of the aminocresol than from the aminocresol itself. Fusion of this benzal derivative with sulfur gave a resin from which no thiazole could be isolated.

3-Hydroxy-6-salicylalaminotoluene.—When a mixture of 10 g. of 3-hydroxy-6-aminotoluene hydrochloride, 0.5 g. of sodium bisulfite, 7.6 g. of salicylaldehyde and 200 cc. of water was vigorously shaken, a voluminous yellow precipitate separated. An aqueous solution of sodium acetate (6 g. of $C_2H_3O_2Na$) was added and the mass again vigorously agitated, when its color changed rapidly from yellow to a reddish orange. The precipitate was collected, washed with water and dried; yield, practically that calculated. Recrystallized from 60% alcohol, it formed red blades, m. p. 92.5" (corr.), soluble in alcohol, ether, benzene or acetic acid, nearly insoluble in water.

Anal. Calcd. for $(C_{14}H_{13}O_2N)_4\cdot C_2H_6O$: C, 72.95; H, 6.13. Found: C, 72.97; H, 6.19.

---

[11] Staedel and Kolb, *Ann.,* 259, 217 (1890).

These analytical results indicate the presence of alcohol of crystallization. The product was therefore recrystallized from carbon tetrachloride until the m. p. remained constant at 111–111.5° (con.).

Anal. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77. Found: C, 73.35, 73.30; H, 5.75, 5.75.

Long drying of these crystals at 105° caused some decomposition. Fusion of this compound with sulfur failed to yield any thiazole.

3-Hydroxy-6-acetylaminotoluene.—A solution of 5 g. of the aminocresol in 150 cc. of water was added to one of 10 cc. of acetic anhydride in 2 cc. of glacial acetic acid, the mixture heated to boiling and filtered hot. Ten g. of Norite was added to the filtrate, which was evaporated on the steam-bath to half its volume, filtered and the filtrate allowed to cool. Radiating clusters of leaflets separated, m. p. 80.5° (corr.); yield, 65–70%. This is the mono-hydrate obtained previously by Staedel and Kolb,[11] who carried out the acetylation by the action of acetic anhydride upon the dry base, a less convenient method of preparation. It loses its water above 110° with formation of the anhydrous amide, m. p. 125°.

Its formation is in agreement with the observation of Lumière and Barbier[12] that the acetylation of aminophenols by acetic anhydride in the presence of water gives only the amide.

3-Hydroxy-6-chloro-acetylaminotoluene was prepared by following the procedure used by Jacobs and Heidelberger[13] for the production of the chloro-acetamide of *p*-aminophenol. The crude product (m. p. 121°; yield, 15%) was recrystallized from a benzene–alcohol (95:5) mixture, until the m. p. remained constant at 133–133.5° (corr.). The pure compound formed pale brownish, irregular plates, soluble in alcohol or hot water but only slightly soluble in benzene.

Anal. Calcd. for $C_9H_{10}O_2NCl$: C, 54.16; H, 5.05. Found: C, 53.91; H, 5.17

Phthal-*p*-hydroxy-*o*-tolil.—A mixture of 3-hydroxy-6-aminotoluene (10 g.), phthalic anhydride (12.1 g.) and benzene (100 cc.) was refluxed for an hour, the solvent then distilled off, the residual gummy mass dissolved in hot 95% alcohol (20 cc.) and the solution cooled. The crystals so obtained were recrystallized from 50% acetic acid, in the presence of Norite, and finally from 95% alcohol. The pure compound formed colorless, fine, short needles, m. p. 204° (corr.); yield, 33%.

Anal. Calcd. for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.38. Found: C, 70.90; H, 4.48.

3-Acetyloxy-6-acetylaminotoluene.—After refluxing for an hour a mixture of 100 g. of the aminocresol with 100 cc. of glacial acetic acid, 10 g. of fused sodium acetate and 85 g. of acetic anhydride were added and the refluxing was continued for another hour. The excess of acid (100–125 cc.) was distilled off, 300 cc. of water and 20 g. of Norite added to the residue, the mixture boiled vigorously for a short time and filtered. As the filtrate cooled, long colorless needles separated which were purified by recrystallization from water and then melted at 127.5–128° (corr.); yield, 75%.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.77; H, 6.28. Found: C, 63.96; H, 6.15.

Nitration of this compound yielded the 5-nitro-acetylamino acetate, unless the reaction was carried out in such a way as to cause some hydrolysis of the acetoxy group, when the 2,4-dinitro-acetylamino *m*-cresol was formed also.

---

[12] Lumière and Barbier, Bull. *soc. chim.*, [3] **33**, 783 (1905).

[13] Jacobs and Heidelberger, THIS JOURNAL, 41,458 (1919).

It dissolved in ether. In water it was less soluble than the hydroxyacetylaminotoluene, but more so than *m*-aminocresol itself. In dilute alkali it dissolved but slowly to a yellow solution which, when neutralized with hydrochloric acid and concentrated, gave the mono-acetyl derivative in a yield almost equal to that calculated. Its aqueous or alcoholic solution was not colored by the addition of ferric chloride.

The same product was obtained by the action of acetic anhydride upon the hydroxyacetylaminotoluene.

2,4-Dichlorotoluquinone-6-acetimide.—A cooled aqueous solution of calcium hypochlorite was poured into an ice cold solution of 3-hydroxy-6-acetylsminotoluene (20 g.) in glacial acetic acid (50 cc.) as long as it caused a precipitate. This yellowish-gray deposit, which gradually became brown and resinous, was collected, washed, dried and extracted with hot carbon tetrachloride. As these extracts cooled, crystals separated which, after repeated crystallization from ether, formed long, yellowish needles, m. p. 159–159.5' (corr.); yield of pure product, 25%.

Anal. Calcd. for $C_9H_7O_2NCl_2$: C, 46.59; H, 3.04. Found: C, 46.20; H, 3.03.

2,4-Dichlorotoluquinone.—The above toluquinone acetimide (1 g.), after standing for an hour with cold dilute chromic acid mixture, was distilled with steam. The quinone which passed over, when crystallized from 30% alcohol, formed golden scales, m. p. 104° (corr.), thus agreeing in crystalline form and m. p. with the reports of Southworth[14] and of Raiford,[15] who prepared the compound in other ways.

2,4-Dichloro-3-hydroxy-6-acetylaminotoluene.—Reduction of the dichlorotoluquinone acetimide was accomplished by passing a slow stream of sulfur dioxide through its suspension in dilute alcohol until the yellow color was discharged. The mixture was warmed with sufficient alcohol to effect solution and filtered hot. As the filtrate cooled, short, colorless needles separated, m. p. 212–212.5° (corr.). Raiford,[15] who prepared the compound by acetylation of the dichloro-aminocresol, found a m. p. of 204–207° (uncorr.) on an impure product.

Anal. Calcd. for $C_9H_9O_2NCl_2$: C, 46.20; H, 3.88. Found: C, 46.29; H, 3.92.

3-Hydroxy-5-nitro-6-acetylaminotoluene.—henitro-acetylaminocresyl acetate described beyond was warmed below 70° with a potassium carbonate solution (1 g. of anhydrous potassium carbonate to 20 cc. of water) until all was dissolved. The resultant red solution was neutralized immediately and carefully with acetic acid and the solution cooled. The greenish-yellow blades which separated were removed, and addition of a few drops of acetic anhydride to the red mother liquor discharged the color and separated a few more of the crystals; total yield, 62%. Recrystallized from 30% alcohol, this product formed greenish-yellow plates, m. p. 188.5° (corr.). Mixed with the initial nitro-acetate, the m. p. was lowered to 150–155°.

Anal. Calcd. for $C_9H_{10}O_4N_2$: C. 51.45; H, 4.80. Found: C, 51.24; H, 4.82.

Treated with strong mineral acids, this amide formed red, viscous oils and gums and no simple hydrolysis was realized.

The use of caustic in place of carbonated alkali in the initial hydrolysis caused deeper seated changes and decomposition, accompanied by the evolution of ammonia.

3-Acetyloxy-5-nitro-6-acetylaminotoluene.—The acetylaminocresyl acetate (15 g.)

---

[14] Southworth, *Ann.*, 168, 270 (1873).

[15] Raiford, THIS JOURNAL, 36, 670 (1914).

was added in small portions to a solution of 15 cc. of fuming nitric acid (sp, gr. 1.6) in 25 cc. of acetic anhydride, while the temperature was maintained below 5°. After the addition of all the acetate, the mixture was left in the freezing mixture for an hour. Crushed ice (300 g.) was then added and the mixture allowed to warm up gradually to laboratory temperature. The fine, yellow precipitate of crude nitro derivative amounted to a yield of 93%. Recrystallized from 50% acetic acid, it formed pale tan blades, m. p. 190–190.5° (corr.).

Anal. Calcd, for $C_{11}H_{12}O_5N_2$: C, 52.38; H, 4.76. Found: C, 52.52; H, 4 90.

The properties of this compound are quite different from those of the 3-acetyloxy-2-nitro-6-acetylaminotoluene described by Brand and Zoller.[16]

In the mother liquors some 3-hydroxy-2,4-dinitro-6-acetylaminotoluene was found, the amount being small unless the nitration was carried out in such manner as to cause considerable hydrolysis of the acetoxy group.

3-Hydroxy-2,4-dinitro-6-aminotoluene.—The dinitro-acetylaminocresol (1 g.) was boiled with concentrated hydrochloric acid (20 cc.) and water (30 cc.) until all was dissolved. The solution was decolorized with Norite, the filtrate from which yielded irregular, pale yellow plates on cooling. These plates lost hydrochloric acid gradually when heated and decomposed very rapidly at 200°.

Anal. Calcd. for $C_7H_7O_5N_3 \cdot HCl$: Cl, 14.20. Found: Cl, 14.34.

The free base was obtained by neutralizing with ammonia the mother liquors from the above hydrochloride and then adding a slight excess of acetic acid. The base precipitated as a red powder, which crystallized from 50% alcohol in blood-red blades, m. p. 166.5–167.5° (corr.). Nietzki and Ruppert,[17] who prepared this compound by the nitration of amino-cresotinic acid ($CH_3,OH,COOH,NH_2 = 1,3,4,6$), gave its m. p. as 160". It is but slightly soluble in water.

Anal. Calcd. for $C_7H_7O_5N_3$: C, 38.54; H, 3.24. Found: C, 38.57; H, 3.60.

3-Hydroxy-2,4-dinitro-6-acetylaminotoluene.—The acetylaminocresol (30 g.) was dissolved in the minimum quantity of glacial acetic acid and added dropwise to a well-cooled mixture of fuming nitric (sp. gr. 1.5) (45 g.) and glacial acetic (15 g.) acids, at such a rate that the temperature was maintained below 5°. After this addition had been completed, the mixture was left in the ice pack for two hours longer and was then poured upon 200 g. of crushed ice. The crude dinitro derivative separated as a yellow powder (yield, 50%), which was removed, washed with water and crystallized from glacial acetic acid, when it formed twinned orange-yellow plates, melting with decomposition at 231° (corr.), somewhat soluble in water.

Anal. Calcd. for $C_9H_9O_6N_3$: C, 42.37; H, 3.56. Found: C, 42.53; H, 3.62.

This method is a modification of that used by Reverdin and Crépieux[18] for the nitration of o-acetotoluidide.

By a different method, employing an acetylamino-m-cresotinic acid as initial material, Nietzki and Ruppert[19] have prepared this same compound and record an uncorrected m. p. of 225°.

---

[16] Brand and Zoller, *Ber.*, 40, 3332 (1907).

[17] Nietzki and Ruppert, ibid., **23,** 3479 (1890).

[18] Reverdin and Crépieux, *ibid.*, 33, 2498 (1900).

[19] Nietzki and Ruppert, *ibid.*, **23,** 3478 (1890).

3-Acetyloxy-2,4-dinitro-6-acetylaminotoluene.—After refluxing for four hours a solution of 0.7 g. of the dinitro-acetylaminocresol and a small amount of fused sodium acetate in 5 cc. of glacial acetic acid and 5 cc. of acetic anhydride, the mixture was cooled, diluted with 10 cc. of water, 0.5 g. of Norite added, the refluxing continued for another hour and the mixture filtered hot. As the filtrate cooled, yellowish-green needles separated which were crystallized from 50% alcohol and then melted at 170–170.5° (corr.); yield of pure product, 75%.

Anal. Calcd. for $C_{11}H_{11}O_7N_3$: C, 44.44; H, 3.73. Found: C, 44.40; H, 3.80.

The product was only slightly soluble in water, and its aqueous solution was not colored by the addition of ferric chloride. Nietzki and Ruppert[17] recorded a m. p. of 175° for a diacetyl derivative prepared by the action of acetic anhydride upon the dinitro-aminocresol but gave no analytical figures.

3-Ethoxy-4-nitrotoluene.—The ethoxynitrotoluidine (1 g.) was dissolved in boiling alcohol (20 cc.) and diazotized by adding slightly more than the calculated amount of sulfuric acid and then introducing slowly into the interior of the liquid, by means of a funnel tube, the calculated amount of nitrite dissolved in the minimum quantity of water. The mixture was boiled for five minutes, cooled, concentrated under reduced pressure and the gummy residue distilled with steam. The yellow solid carried over by the steam, crystallized from petroleum ether, gave tan needles (0.3 g.), m. p. 51–51.5°. Staedel and Kolb,[20] who prepared this compound from the silver salt of the nitrocresol and ethyl iodide reported a m. p. of 50–51°.

3-Ethoxy-6-aminotoluene.—When 3-ethoxy-6-benzalaminotoluene (100 g.) was mixed with dilute (50 cc. of concentrated acid to 600 cc. of water) hydrochloric acid. and the mixture distilled with steam as long as benzaldehyde came over, 70% of the calculated amount of aldehyde was collected. The red solution remaining in the distilling flask was neutralized with the calculated amount of sodium hydroxide and a red oil separated, which was collected and distilled, the major fraction coming over at 253–255° as a pale yellow oil which slowly darkened; yield, 83%.

Anal. Calcd. for $C_9H_{13}ON$: C, 71.50; H, 8.67. Found: C, 71.42; H, 8.46.

The compound was only very slightly soluble in water. Staedel and Kayser[21] obtained the same compound by reduction of the corresponding nitrocresyl ether, but merely stated that it resembled in general the corresponding *o*-cresol derivative and was volatile with steam. They also prepared and analyzed its oxalate.

Hydrochloride.—Colorless, large, flat plates, which began to decompose above 200° and melted finally at 212° (corr.); soluble in water or in alcohol.

Anal. Calcd. for $C_9H_{13}ON{\cdot}HCl$; Cl, 18.90: Found, 18.94.

3-Ethoxy-6-benzalaminotoluene.—One mole (10 g.) of 3-hydroxy-6-benzalaminotoluene was ground up with 1.05 moles (1.1 g.) of sodium hydroxide and 2.5 cc. of 95% alcohol. The heat evolved was sufficient to drive off the water and alcohol, leaving a greenish-gray powder. This powder was mixed with 20 cc. of 95% alcohol and 1.5 moles (7.8 cc.) of ethyl bromide, and the mixture refluxed for three hours, after which the alcohol and excess ethyl bromide were evaporated, 100 cc. of water was added to the residue, the heavy red oil which separated was removed and the residual liquid extracted with 20 cc. of benzene to recover the rest of this oil. The oil was washed carefully

---

[20] Staedel and Kolb, *Ann.*, 259,224 (1890).

[21] Staedel and Kayser, ibid., 217,219 (1883).

(to avoid emulsions) thrice with 0.5 N sodium hydroxide solution and then with water to remove the alkali. The washed oil was diluted with benzene (100 cc.), the solution dried over anhydrous sodium sulfate and distilled under diminished pressure, collecting the fraction of b. p. 212–217° (20 mm.); yield, 80%. The product was a bright yellow oil which gradually turned red on standing. It was soluble in alcohol, ether or benzene but not in water or alkalies.

Anal. Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.17. Found: C, 79.66, 79.58; H, 7.17, 7.15.

The same product was obtained when the ethylation was effected with ethyl sulfate instead of ethyl bromide.

The sodium salt of the aminocresol was dried thoroughly at 100–110°, the dry powder stirred slowly into the calculated amount of ethyl sulfate, the mixture heated at 100° for three hours, then diluted with water, the heavy oil separated and treated as described above; yield, 50%, of a product boiling at 210–217° (20 mm.). No thiazole was obtained when this benzal derivative was fused with sulfur.

3-Ethoxy-6-salicylaminotoluene.—When a mixture of 10 g. of 3-ethoxy-6-aminotoluene hydrochloride, 5 g. of sodium acetate, 100 cc. of water and 6.5 *g.* of salicylaldehyde was shaken vigorously, a heavy, yellow oil separated. This was removed and distilled under reduced pressure, collecting the fraction of b. p. 237–238° (16 mm.). On long standing this fraction crystallized in yellow blades which were purified by dissolving them in an ether--alcohol (4:1) mixture and allowing the solvent to evaporate spontaneously. The yellow solid obtained was readily freed from mother liquor by pressing and melted at 48.5° (corr.).

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.28; H, 6.72. Found: C, 75.50; H, 6.57.

Attempts to prepare a thiazole by fusion of this salicylal derivative with sulfur proved unsuccessful.

3-Ethoxy-6-acetylaminotoluene.—A mixture of 5 g. of the acetylaminocresol, 1.6 g. of sodium hydroxide, 3 cc. of ethyl bromide and 150 cc. of 95% alcohol was refluxed for ten hours, the alcohol then distilled off, the residue dissolved in the minimum quantity of hot 20% alcohol, the solution filtered and the filtrate cooled. The crystals which separated, after repeated recrystallization and decolorization, appeared as glistening, colorless needles, m. p. 118.5" (corr.); yield, 80–85%. Kayser[22] and Staedel and Kayser,[21] both of whom prepared it by direct acetylation of the aminocresol ethyl ether, gave the m. p. of this compound as 114°.

The solubility of phenacetin itself in 100 parts of water at 25" is stated as 0.077 part,[23] whereas this homolog dissolves to the extent of 0.28 part.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 68.37; H, 7.83. Found: C, 68.36; H, 7.84.

Attempts to oxidize this toluene derivative to the corresponding benzoic acid by the action of potassium permanganate, either alone or in the presence of magnesium sulfate, proved unsuccessful; nor could we convert it into the corresponding benzaldehyde by Bornemann's[24] modification of the Étard reaction.

---

[22] Kayser, Ber., **15**, 1135 (1882).

[23] U. S. Pharmacopoeia, 10th Revision, **1926.**

[24] Bornemann, *Ber.,* **17**, 1462 (1884).

A similar lack of success attended our efforts to convert it into the 2-methyl-5-ethoxy-indole by the action of sodium ethylate or amylate in a reducing atmosphere, according to the method by which Madelung[25] obtained indoles from the acetyl, benzoyl and oxalyl derivatives of *o*-toluidine. Our products were only intractable tars from which no pure compounds were isolated.

3-Ethoxy-6-chloro-acetylaminotoluene.—To a solution of 15 g. of chloro-acetyl chloride in 30 cc. of benzene, there was added slowly 20 g. of 3-ethoxy-6-aminotoluene in 30 cc. of benzene. After a vigorous stirring of the crystal paste, the benzene (and hydrogen chloride) was evaporated, leaving a yield of crude amide about equal to that calculated. By crystallization from dilute acetic acid, the pure compound was secured in colorless, short, matted needles, m. p. 140.5–141° (corr.).

Anal. Calcd. for $C_{11}H_{14}O_2NCl$: C, 58.03; H, 6.20. Found: C, 57.87; H, 6.16.

When this compound was heated with aluminum chloride, following the method of Stollé,[26] no oxindole was obtained, although StollC accomplished this cyclization with **chloro-acetyl-o-toluidide.**

3-Ethoxy-6-salicylylaminotoluene.—When a benzene (20 cc.) solution of salicylic acid (4.6 g.) was added to a simple solution of 3-ethoxy-6-aminotoluene(5 g.) in benzene (30 cc.), and the flask shaken vigorously, the salt separated immediately. Phosphorus oxychloride (4 cc.) was added and the mixture refluxed as long as hydrogen chloride was evolved. The benzene was evaporated and the residue washed with hot water to remove the phosphoric acid. The soft, resinous mass remaining was dissolved in alcohol. Addition of water (50%) to this alcoholic solution, precipitated the crude amide (4 g.). As repeated crystallization from 75% acetic acid failed to give a colorless product, it was dissolved in 1 *N* sodium hydroxide, the alkaline solution digested with Norite for thirty minutes, filtered, the amide reprecipitated by saturating the filtrate with carbon dioxide, the precipitate washed. dried and recrystallized from alcohol. It was thus obtained in fine, colorless needles, m. p. 153.4–154° (corr.).

Anal. Calcd. for $C_{16}H_{17}O_3N$: C, 70.82; H, 6.32. Found: C, 70.74; H, 6.19.

Oxal-*p*-ethoxy-*o*-toluidide.—If a mixture of 10 g. of 3-ethoxy-6-aminotoluene with 5 cc. of ethyl oxalate was refluxed gently for two hours, or until no more condensate dripped back from the condenser, and was then cooled, it congealed to a cake of the crude toluidide (m. p. 200°); yield, 8.5 g., or 72%. Recrystallized from a 1:1 alcohol–benzene mixture, it yielded long, colorless needles, m. p. 205° (corr.), soluble in alcohol, benzene or ether, but not in water.

Anal. Calcd. for $C_{20}H_{24}O_4N_2$: C, 67.39; H, 6.79. Found: C, 67.45; H, 6.95.

As a by-product there was isolated what appeared to be the substituted oxanilic acid ester but the amount was too small for satisfactory purification and identification.

Experiments designed to transform this toluidide into the 5,5′-diethoxydiindyl, by the method of Madelung,[25] yielded only decomposition products.

Phthal-*p*-ethoxy-*o*-tolil.—A solution of 5 g. of 3-ethoxy-6-aminotoluene and 5 g. of phthalic anhydride in 25 cc. of benzene was refluxed for an hour. As the solution

---

[25] Madelung, Ber., 45, 1128 (1912).

[26] Stollé, J. prakt. *Chem.,* [2] 105, 137 (1923).

cooled, crystals separated which were recrystallized from 80% alcohol until colorless needles were obtained of the constant m. p. 140.5° (corr.); yield, 75%.

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.57; H, 5.38. Found: C, 72.07; H, 5.27.

Ethyl (2-Methyl-4-ethoxyphenyl)-acetylglycinate.—To a solution of 12 g. of 3-ethoxy-6-acetylaminotoluene in 50 cc. of dry benzene, there was added 1.5 g. of metallic sodium and the mixture was refluxed until the sodium had all reacted. At thirty to sixty-minute intervals three portions of ethyl chloro-acetate were added, amounting in all to 10 g., after which the mixture was refluxed for two to three hours longer, cooled, 10 cc. of water added to dissolve the salt formed, the benzene layer separated, the aqueous layer extracted twice more with benzene, the benzene extracts united, dried with anhydrous sodium carbonate and distilled, at first under atmospheric and finally under reduced pressure. A yellow, viscous oil was obtained, b. p. about 210° (15 mm.) which, after repeated rectification, yielded a fraction, b. p. 210–212.5° (22 mm.); yield, 10 g. or 60%.

Anal. Calcd. for $C_{15}H_{21}O_4N$: C, 64.51; H, 7.58. Found: C, 64.25; H, 7.34.

The above procedure is similar to that employed by Paal and Otten[27] for the production of ethyl acetanilido-acetate.

According to a recent German patent,[28] it should be possible to condense such a glycine to an indoxyl and to oxidize this indoxyl to the corresponding indigo but, although we followed the patent specifications closely, this result could not be realized.

2,4-Dichloro-3-ethoxy-6-aminotoluene.—The acetyl derivative (10 g.) was hydrolyzed by refluxing it for four hours with 2 N hydrochloric acid. There resulted a yellow, granular precipitate with red supernatant solution. Sufficient hot water was added to bring all into solution and the color was removed by digesting the solution with Norite. As the filtrate from this Norite cooled, it deposited long, colorless blades of the hydrochloride, which lost hydrochloric acid slowly and turned pinkish. They began to darken at 220° and melted at 244° (corr.).

Anal. Calcd. for $C_9H_{11}ONCl_2 \cdot HCl$: Cl, 13.82. Pound: Cl, 13.78.

The free amine was obtained by the addition of solid ammonium carbonate to a solution of the above hydrochloride and was purified by crystallization from 20% alcohol. It formed irregular plates and scales, m. p. 83° (corr.).

Anal. Calcd. for $C_9H_{11}ONCl_2$: C, 49.11; H, 5.04. Found: C, 49.44, 49.43; H, 5.18, 5.16.

2,4-Dichloro-3-ethoxy-6-acetylaminotoluene.—Bender's[6] procedure for the chlorination of acetanilide was modified as follows.

A hypochlorite solution was prepared from 127 g. (one mole) of calcium hypochlorite and 84 g. (one mole) of sodium bicarbonate in 1 liter of water, which was agitated frequently during three or four hours, then left overnight and finally filtered. This filtrate was added gradually to a cold solution of 10 g. of 3-ethoxy-6-acetylaminotoluene in 30 cc. of glacial acetic acid as long as it caused a precipitate. This required about 200 cc. The amorphous precipitate was crystallized from 50% acetic acid until its

---

[27] Paal and Otten, *Ber.*, 23, 2594 (1890).

[28] Badische Anilin- und Soda Fabrik, German Patent 188,436 (1907); *Friedlander*, 4, 514.

m. p. remained constant at 162.5–163° (corr.); yield, 10 g. or 75%. The product was soluble in alcohol, benzene or acetic acid, but dissolved very slightly in water.

Anal. Calcd. for $C_{11}H_{13}O_2NCl_2$: C, 50.40; H, 5.00. Found: C, 50.23; H, 5.08.

The same product was obtained by the action of sodium ethoxide and ethyl iodide upon 3-hydroxy-2,4-dichloro-6-acetylaminotoluene.

3-Ethoxy-4-nitro-6-aminotoluene.—When the acetyl derivative of this compound (1 g.) was boiled in 6 *N* hydrochloric acid until solution was complete and this solution was then allowed to cool, colorless plates of the hydrochloride separated which began to darken at 240° and decomposed at 249'. This salt was better defined and more stable than the 5-nitro isomer.

Anal. Calcd. for $C_9H_{12}O_3N_2 \cdot HCl$: Cl, 15.24. Pound: Cl, 15.28.

Neutralization of the mother liquors yielded the free base, which crystallized from 30% alcohol in dark red, columnar form, m. p. 86–87" (corr.).

Anal. Calcd. for $C_9H_{12}O_3N_2$: C, 55.09; H, 6.17. Found: C, 54.91; H, 6.23.

3-Ethoxy-4-nitro-6-acetylaminotoluene.—A solution of 20 g. of the acetylamino cresyl ether in the minimum amount of glacial acetic acid was added very slowly to a well-cooled solution of 20 g. of fuming (sp. gr. 1.5) nitric in 20 cc. of glacial acetic acid, so that the temperature never rose above 0°. After standing for two hours at 0°, the mixture was poured upon 200 g. of crushed ice, the yellow precipitate collected (yield, 55%), washed, dried and recrystallized from 95% alcohol, when it formed yellow plates, m. p. 192.5–193° (corr.).

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.47; H, 5.93. Found: C, 55.62; H, 5.93.

The mother liquor from these crystals contained also the 5-nitro isomer (m. p. 160°) to the extent of 10–15% of the total yield. It was separated from the 4-nitro form by fractional crystallization from 20% alcohol, in which solvent the 4-nitro derivative is the less soluble.

The 5-nitro derivative separated in this reaction was identical in all respects with that prepared by the ethylation of the 5-nitro-acetylaminocresol.

3-Ethoxy-5-nitro-6-aminotoluene.—The acetyl derivative of this base was hydrolyzed easily by concentrated hydrochloric acid, forming a red solution from which but little of the hydrochloride separated. The small amount obtained appeared in tan-colored fibers which began to darken above 200°, resinified at about 220°, and decomposed at about 240°.

Anal, Calcd. for $C_9H_{12}O_3N_2 \cdot HCl$: Cl, 15.34. Found: Cl, 14.87.

This salt was rapidly hydrolyzed by water to the free base, which crystallized from 30% alcohol in long orange-red needles, m. p. 101–101.5' (corr.).

Anal. Calcd. for $C_9H_{12}O_3N_2$: C, 55.09; H, 6.17. Found: C, 54.93; H, 6.31.

3-Ethoxy-5-nitro-6-acetylaminotoluene.—Metallic sodium (0.3 g.) was dissolved in absolute alcohol (20 cc.), the nitro-acetylaminocresol (1 g.) was added, followed by ethyl iodide (5 cc.), and the mixture was refluxed until its color changed from red to yellow (about two hours). Water (20 cc.) and Norite (1 g.) were added, the mixture boiled for ten minutes and filtered hot. As the filtrate cooled the crude ethoxy derivative separated in yellow needles which melted at 160° (corr.) after recrystallization from 50% alcohol; yield of crude product, 85%.

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.47; H, 5.93. Found: C, 55.56; H, 5.88.

By crystalline form, color and mixed m. p., this compound was proved to be identical with the 5-nitro derivative prepared by direct nitration of the ethoxyacetylaminotoluene.

The failure of our attempts to reduce this nitro derivative to the amine is in agreement with the observations of Bogert and Taylor[29] on the reduction of 3-nitro-4-acetylaminophenetole, and is in further support of the assumption that the nitro is adjacent to the acetylamino group.

3-Ethoxy-2,4-dinitro-6-aminotoluene.—The acetyl derivative of this compound (1 g.) was refluxed for three hours with 6 *N* hydrochloric acid (30 cc.) and Norite (1 g.), and filtered hot. The hydrochloride of the base separated, as the filtrate cooled, in pale yellow, rectangular plates which began to darken above 140° and decomposed at 195–197°.

Anal. Calcd. for $C_9H_{11}O_5N_3 \cdot HCl$: Cl, 12.77. Found: Cl, 12.85.

The mother liquors from the hydrochloride, when treated with ammonia, precipitated the free base as a yellow, flocculent solid which crystallized from 10% alcohol in short, yellow needles, m. p. 96–97" (corr.).

Anal. Calcd. for $C_9H_{11}O_5N_3$: C, 44.82; H, 4.60. Found: C, 44.70; H, 4.70.

3-Ethoxy-2,4-dinitro-6-acetylaminotoluene.—The dinitro-acetylaminocresol (5 g.) was ground in a mortar with anhydrous sodium carbonate (2.5 g.) and a little water (0.5 cc.). The brownish red triturate, after thorough drying, was heated with ethyl sulfate (5 cc.) at 140° for an hour, then cooled, water (50 cc.), alcohol (20 cc.) and Norite (1 g.) were added, the mixture was boiled for a short time and filtered hot. As the filtrate cooled, the ethoxy derivative separated. It was collected and crystallized from 50% alcohol, when it appeared in long, pale yellow needles, m. p. 167–167.5° (corr.); yield, 76% (2.5 g.), calculated on unrecovered cresol, since 30% of the initial material was recovered by acidification of the mother liquors from the crude product.

Anal. Calcd. for $C_{11}H_{13}O_6N_3$: C, 46.65; H, 4.63. Found: C, 46.89; H, 4.74.

3-Ethoxy-4,5-dinitro-6-acetylaminotoluene was prepared by the direct nitration of the ethoxy-acetyltoluidide, by the method of Blanksma,[10] for the analogous phenacetin derivative, following the modifications later suggested by Bogert and Taylor;[29] yield 67%. It crystallized from 95% alcohol in pale yellowish, fine needles, m. p. 257–258° (corr.).

The same product was obtained by subjecting the ethoxy-4-nitro-acetyltoluidide to a similar treatment; yield. 85%. It was insoluble in water and only slightly soluble in alcohol or glacial acetic acid.

Anal. Calcd. for $C_{11}H_{13}O_6N_3$: C, 46.68; H, 4.63. Pound: C, 46.54; H, 4.74.

3-Ethoxy-4,6-diacetylaminotoluene.—When 2 g. of the 4-nitro-ethoxyacetotoluidide was reduced with stannous chloride in hydrochloric acid solution until the yellow color of the solution was discharged, and the tin was then precipitated by hydrogen sulfide, the filtrate darkened so rapidly in the air that the excess of acid was neutralized with sodium carbonate and 5 cc. of acetic anhydride was added; yield of crude product, 57%. It crystallized from 10% alcohol in colorless, short, matted needles, m. p. 200–200.5° (corr.).

Anal. Calcd. for $C_{13}H_{18}O_3N_2$: C, 62.40; H, 7.25. Found: C, 62.09; H, 7.47.

3-Ethoxy-3'-hydroxy-6,6'-azotoluene.—To the solution of the diazonium chloride obtained by diazotizing at 0° 20 g. of 3-ethoxy-6-aminotoluene, there was added a cold

---

[29] Bogert and Taylor, THIS JOURNAL, **49,** 1578 (1927).

solution of 11.5 g. of m-cresol and 15 5 g. of hydrated sodium carbonate in 100 cc. of water. After standing overnight, the tarry precipitate became crystalline. It was removed, washed, dried and crystallized from benzene, when it appeared in long brownish spikes, m. p. 132.5° (corr.); yield, 60%.

Anal. Calcd. for $C_{16}H_{18}O_2N_2$: C, 71.09; H, 6.71. Found: C, 71.15; H, 6.71.

3,3′-Diethoxy-6,6′-azotoluene.—To 300 cc. of absolute alcohol in which 3 g. of metallic sodium had been dissolved, there was added 25.5 g. of 3-ethoxy-3′-hydroxy-6,6′-azotoluene, followed by 25 g. of ethyl bromide. The mixture was allowed to stand overnight and was then refluxed for six hours. The crystals which separated as the solution cooled were ground up in water, to remove all sodium salts, dried and crystallized from benzene. The compound separated in yellow, granular crystals, m. p. 149–149.5° (corr.); yield, 62%.

Anal. Calcd. for $C_{18}H_{22}O_2N_2$: C, 72.46; H, 7.44. Found: C, 72.61; H, 7.60.

3-Hydroxyethoxy-6-acetylaminotoluene.—After dissolving 5 g. of metallic sodium in 200 cc. of absolute alcohol, the solution was well cooled and 35 g. of the acetylaminocresol hydrate was gradually stirred in until all was dissolved. To this solution there was added 20 g. (125% of that calculated) of ethylene chlorohydrin. The mixture was left for twelve hours in a closed vessel at laboratory temperature and was then refluxed for six hours, the alcohol distilled off, 200 cc. of water added to the residue and the mixture again evaporated. A resinous oil separated and gradually congealed. It was treated with hot 95% alcohol, filtered from the sodium chloride and the filtrate as it cooled deposited crystals. By concentration of the mother liquor a second crop of crystals was obtained. Addition of acetone to this second mother liquor precipitated a third crop. These various lots of crystals were combined and recrystallized. From acetone small granular crystals were secured; from water rhomboidal striated plates and blades; yield of purified product, 25%. Both forms melted at 117–117.5° (corr.).

Anal. Calcd. for $C_{11}H_{15}O_3N$: C, 63.16; H, 7.23. Found: C, 62.92; H, 7.11.

In one hundred parts of water at 25° it dissolved to the extent of 4.35 parts.

3-Acetyloxyethoxy-6-diacetylaminotoluene.—The 3-hydroxyethoxy-6-acetylaminotoluene (3.5 g.) and a little sodium acetate were dissolved in acetic anhydride (3 cc.), the excess of anhydride distilled off, the residual solid dissolved in the minimum quantity of hot 30% alcohol, the solution cooled and the crystals which separated recrystallized from the same solvent. The product appeared as fine, colorless needles, m. p. 117° (corr.). Mixed with some of the initial hydroxyethoxy derivative (m. p. 117–117.5°, corr.), the m. p. was 95–109".

Anal. Calcd. for $C_{15}H_{19}O_5N$: C, 61.42; H, 6.52. Found: C, 61.52; H, 6.58.

Summary

1. 3-Hydroxy-6-aminotoluene has been studied as a possible source of useful intermediate or final products.

2. Since it is a homolog of *p*-aminophenol, various new derivatives have been prepared, analogous structurally to such well-known drugs as Phenacetin, Pertonal, Malakin and the like, but the pharmacological properties of these new products have not been determined as yet.

3. Chlorination and nitration of both the hydroxy and the corresponding ethoxy derivatives have been investigated, as well as the reduction products of the nitro derivatives.

4. In the course of the research many new compounds have been synthesized and many old ones prepared by new methods.

5. It was discovered that the benzalamino derivatives of these *p*-aminophenol types offered a very satisfactory form in which to ethylate the phenolic hydroxyl group.

NEW YORK, N. Y.

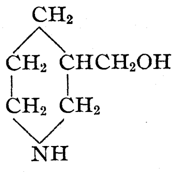
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

LOCAL ANESTHETICS DERIVED FROM 2-(BETA-HYDROXYETHYL)-PIPERIDINE

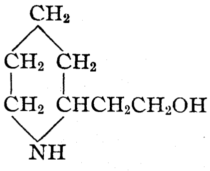
BY C. S. MARVEL AND R. S. SHELTON

RECEIVED NOVEMBER 5, 1928 PUBLISHED MARCH 6, 1929

Recently Sandborn and Marvel[1] have prepared the paminobenzoates of certain N-alkyl derivatives of β-piperidylcarbinol and have found that their monohydrochlorides have a strong local anesthetic action combined with a low toxicity. The close structural relation between β-piperidylcarbinol (3-hydroxymethylpiperidine) (I) and 2-(β-hydroxyethyl)-piperidine (II) suggested that similar derivatives of this second amino alcohol might have desirable pharmacological action.



I



II

The starting material for the preparation of these compounds is a-picoline. By the procedure of Ladenburg[2] this with formalin gave 2-(β-hydroxyethyl)-pyridine, which was reduced to the piperidine derivative by means of sodium and alcohol.[3] The nitrogen atom was alkylated by treatment with the corresponding alkyl halide, following the general method used to alkylate β-piperidylcarbinol.[4] These tertiary amino alcohols were treated with *p*-nitrobenzoyl chloride to give the corresponding ester hydrochlorides, which were in turn reduced catalytically by means of hydrogen and the platinum catalyst of Adams and Shriner[5] to the amino ester hydrochlorides. This reduction gave the best product when glacial acetic acid was used as a solvent. When alcohol was used as a solvent a colorless product was obtained at first but on standing it turned red. When

---

[1] Sandborn and Marvel, THIS JOURNAL, 50,563 (1928).

[2] Ladenburg, *Ber.*, 43,2378 (1910).

[3] Ladenburg, *Ann.*, 301, 129 (1898).

[4] Ref. 1, p. 566.

[5] Adams and Shriner, THIS JOURNAL, 45,2171 (1923).

the reduction was carried out in glacial acetic acid the product remained colorless.

The pharmacological tests were made by Messrs. H. J. Cannon and H. C. Spruth at the Abbott Laboratories,[6] using a 1% solution of the monohydrochloride of each amino ester on the cornea of a rabbit to determine the onset and duration times. Toxicity was determined by intravenous injection in rabbits.

TABLE I

PHARMACOLOGICAL PROPERTIES

Alkyl group	Ethyl	n-Propyl
Average onset, minutes	3	2.25–2.5
Av. duration of anesthesia, min.	15–20	35-40
M.F.D., mg. per kg. of body wt.	Not determined	14–15

It is interesting to note that the difference in structure between these derivatives and those from β-piperidylcarbinol is sufficient to reduce considerably their local anesthetic action. The α-derivatives are slower in their onset time and act for a shorter time than the β-derivatives.

Experimental Part

2-(β-Hydroxyethyl)-piperidine.—From 23 g. of a-picoline and 33 g. of technical formalin heated in sealed tubes at 135° for twelve to fourteen hours, there was obtained 6–7 g. of 2-(β-hydroxyethyl)-pyridine. Reduction of 23 g. of this pyridine derivative with 93 g. of sodium and 1 liter of absolute alcohol gave 13 g. of 2-(β-hydroxyethyl)-piperidine (b. p. 145–146° at 36 mm.). If care was not taken completely to remove the sodium hydroxide solution from the amino alcohol before distillation, there was considerable loss of material due to decomposition.

N-Alkyl 2-(β-Hydroxyethyl)-piperidines.—In a 250-cc. three-necked flask fitted with a condenser, a separatory funnel and a mechanical stirrer, was placed a benzene solution of the amino alcohol, and to it was added from the separatory funnel the alkyl halide. For the methyl derivative methyl iodide was used and the mixture was stirred

TABLE II

PREPARATION AND PROPERTIES OF N-ALKYL 2-(β-HYDROXYETHYL)-PIPERIDINES

Alkyl	Halide, g.	Amino alcohol, g.	N-alkyl yield, g.	B. p., °C.	d_4^{20}	n_D^{20}
Methyl	21	19.5	10	175–178 (35–40 mm.)	0.9840	1.4872
Ethyl	6	12.5	10	136 (27–28 mm.)	.9730	1.4885
n-Propyl	7.5	16	13.5	139–141 (27 mm.)	.9657	1.4905

Since the physical constants were not entirely in agreement with those reported by Ladenburg (ref. 3, pp. 133, 137, 140), the amino alcohols were titrated as a check on their purity.

TITRATIONS

Derivative	Taken, g.	0.1001 *N* HCl, cc.	Formula	Neutral equiv. Calcd.	Neutral equiv. Found
Methyl	0.1740	19.25	$C_8H_{17}NO$	143	142.2
Ethyl	.1644	17.04	$C_9H_{19}NO$	157	155.6
n-Propyl	.1950	11.46	$C_{10}H_{21}NO$	171	170

---

[6] The authors desire to express their thanks to Mr. Cannon, Mr. Spruth and the Abbott Laboratories for their assistance in this investigation.

at room temperature for two days. For the ethyl and *n*-propyl derivatives the alkyl bromides were used and the reaction mixtures were heated for eight hours on a steam-bath. A dark gummy material separated from the benzene in each case. The mixture was treated with excess 40% sodium hydroxide solution and the benzene layer was separated. The aqueous layer was extracted once with benzene and the benzene solutions were combined. The benzene was evaporated and the residue was distilled under reduced pressure. The results of the experiments are given in Table II.

N-Alkyl 2-(β-Hydroxyethyl)-piperidine *p*-Nitrobenzoate Hydrochlorides.—These compounds were prepared according to the usual procedure from the amino alcohols and p-nitrobenzoyl chloride in benzene solution.[1] The compounds separated from the solution as thick, gummy products. They were obtained crystalline by dissolving in absolute alcohol and precipitating with anhydrous ether. The methyl and n-propyl derivatives were especially difficult to obtain in a pure condition and the precipitation had to be repeated several times. The yields were about 55–60%. The results of these experiments are given in Table III.

TABLE III

PROPERTIES AND ANALYSES OF N-ALKYL 2-(β-HYDROXYETHYL)-PIPERIDINE *p*-NITROBENZOATE HYDROCHLORIDES

Alkyl group	M. p., °C.	Subs., g.	0.0549 N AgNO₃, cc.	Empirical formula	Chlorine, % Calcd.	Chlorine, % Found
Methyl	181–182	0.1075	5.88	$C_{15}H_{21}N_2O_4Cl$	10.78	10.66
Ethyl	198–199	.1155	6.13	$C_{16}H_{23}N_2O_4Cl$	10.35	10.34
n-Propyl	124–126	.1020	5.18	$C_{17}H_{25}N_2O_4Cl$	9.94	9.90

N-Alkyl 2-(β-Hydroxyethyl)-piperidine *p*-Aminobenzoate Hydrochlorides.—To a solution of 5 g. of the nitrobenzoyl ester hydrochloride in 200 cc. of solvent was added 0.25 g. of platinum oxide catalyst[6] and the mixture was shaken with hydrogen under about two atmospheres' pressure for about forty-five minutes. The drop in pressure indicated that reduction was complete in about seven minutes. The mixture was filtered to remove the catalyst and the solvent was evaporated. The residue was dissolved in about 75 cc. of absolute alcohol and then about 300 cc. of anhydrous ether was added to precipitate the product. This operation was repeated as often as was necessary to obtain a pure product. When the solvent was absolute alcohol, a nearly colorless product was obtained which turned red on standing. The ethyl derivative was made using this solvent. Glacial acetic acid was used as a solvent for the reduction of the propyl derivative and a better grade of material was obtained, although it was quite difficult to crystallize. The methyl compound has not been obtained in a crystalline form. The properties of the compounds are described in Table IV.

TABLE IV

PROPERTIES AND ANALYSES OF N-ALKYL 2-(β-HYDROXYETHYL)-PIPERIDINE *p*-AMINOBENZOATE HYDROCHLORIDES

Alkyl group	M. p., °C.	Subs., g.	0.1050 N AgNO₃, cc.	Empirical formula	Chlorine, % Calcd.	Chlorine, % Found
Ethyl	238.5–239	0.1034	3.20	$C_{16}H_{25}N_2O_2Cl$	11.33	11.35
n-Propyl	175–176	.1044	3.07	$C_{17}H_{27}N_2O_2Cl$	10.85	10.88

Summary

The monohydrochlorides of the paminobenzoyl esters of N-ethyl- and N-*n*-propyl-2-(β-hydroxyethyl)-piperidine have been prepared and their local anesthetic values have been determined.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE PREPARATION OF SYMMETRICAL METHYL ISOPROPYL HYDRAZINE AND METHYL ISOPROPYL DI-IMIDE

BY HERMAN C. RAMSPERGER[1]

RECEIVED NOVEMBER 5, 1928 PUBLISHED MARCH 6, 1929

The author has recently studied the rate of thermal decomposition of the gases of azomethane[2] (dimethyl di-imide) and azo-isopropane[3] (di-isopropyl di-imide). Their decomposition was found to be homogeneous and unimolecular. A study of the mixed azo compound methyl isopropyl di-imide would be valuable in indicating the mechanism of the decomposition and would provide a further test of various theories of unimolecular reactions. This compound had, however, never been prepared, nor had the corresponding hydrazine from which the azo compound could be prepared by oxidation. The preparation of these two new compounds is the first synthesis reported in the literature of a simple mixed aliphatic symmetrical hydrazine or of a mixed aliphatic azo compound.

A method of preparing the hydrazine derivative was suggested by Lochte, Bailey and Noyes.[4] By this method the hydrazone formed by treating methyl hydrazine with acetone would be reduced with hydrogen and colloidal platinum. This procedure was tried. An impure sample of the hydrazone was obtained but it could not be successfully reduced. In this connection it is significant that the reduction of the azine formed from hydrazine and acetaldehyde with hydrogen and platinum catalyst yields a gummy sirup from which no hydrazine derivative could be recovered. This method works well in the preparation of those symmetrical hydrazine derivatives having isopropyl or heavier radicals. It seems likely, therefore, that catalytic reduction will not succeed as a general method for the preparation of the simpler aliphatic hydrazines.

Preparation of Symmetrical Methyl Isopropyl **Hydrazine.**—The successful method is indicated by the following equations

$$C_3H_7(COC_6H_5)N-NH(COC_6H_5) + (CH_3)_2SO_4 + NaOH = C_3H_7(COC_6H_5)N-N(COC_6H_5)CH_3 + NaHSO_4 + CH_3OH \quad (1)$$

$$C_3H_7(COC_6H_5)N-N(COC_6H_5)CH_3 + 2H_2O = C_3H_7NH-NHCH_3 + 2C_6H_5COOH \quad (2)$$

Dibenzoyl isopropyl hydrazine was prepared by the procedure of Lochte, Bailey and Noyes.[4] This was methylated with methyl sulfate to give dibenzoyl methyl isopropyl hydrazine.

The dibenzoyl isopropyl hydrazine was dissolved in the smallest possible amount of 95% alcohol. To this was added with constant stirring equal molal amounts of

---

[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, 49,912, 1495 (1927).

[3] Ramsperger, *ibid.*, 50, 714 (1928).

[4] Lochte, Bailey and Noyes, *ibid.*, 43,2597 (1921); 44, 2556 (1922).

methyl sulfate and concentrated sodium hydroxide solution. One-fourth of the total amounts of each were separately added and when in about one hour the alkaline solution became acid, another fourth was added and so on, and finally an excess of 10 to 20% was added. A greater excess decreased the yield. The product was precipitated from solution by adding four volumes of water with constant stirring. The yield of crude product was 80% of that calculated. It melts at 63–6S°. It was purified by dissolving in alcohol and adding water, by crystallizing from ether or by dissolving in ether and adding petroleum ether. The yield was reduced to about 70% and the melting point was then 74–76". Several recrystallizations gave a melting point of 76.25 to 76.75'.

The once purified product was hydrolyzed by adding five times its weight of concentrated hydrochloric acid and heating on a steam-bath. Benzoic acid soon separated quantitatively. The benzoic acid was filtered off and the remaining solution was concentrated to a very small volume under reduced pressure. It was not possible to isolate the hydrochloride salt by taking up the sirupy residue with absolute alcohol. It was found later that this was due to the extremely hygroscopic nature of this salt. When pure symmetrical methyl isopropyl hydrazine was dissolved in dry ether and dry ether containing an equivalent amount of hydrogen chloride was added, a salt formed at once but became pasty due to the absorption of water while being rapidly filtered.

The sirupy residue was treated with concentrated sodium hydroxide solution (1 to 1) in the presence of pure nitrogen gas at reduced pressure (5 to 40 cm.). The methyl isopropyl hydrazine forms an upper layer which is distilled into a vessel containing sodium hydroxide sticks. The first container was then sealed off. After about twenty-four hours the upper liquid layer was distilled into a container with aluminum amalgam, after another twenty-four hours into another container with aluminum amalgam and finally fractionally distilled. The temperature and pressure of each distillation were carefully noted. The yield of pure product was 50%.

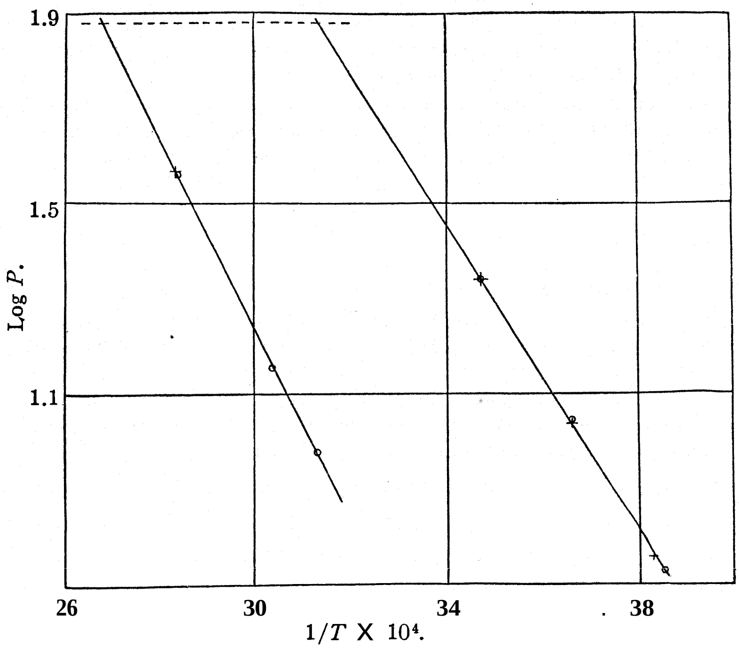
The fractional distillation showed that most of the material distilled between 79.5 and 79.7" at a pressure of 37.1 cm., but the first fourth of it distilled from about 78.0 to 79.5". The lower-boiling fraction probably contained some of the lower-boiling azo compound. Samples of the high-boiling fraction were distilled in vacuum into small bulbs which were used for density determinations and for titrations. Titrations with hydrochloric acid and with iodine by the method of StollC[5] both indicated a purity of 99.7 to 99.8%. The density was 0.7959 ± 0.0005. This value lies between that for symmetrical dimethyl hydrazine (0.8274) and that for symmetrical di-*iso*propyl hydrazine (0.7844). The boiling point under 76 cm. pressure was obtained from the various distillation temperatures and pressures. In Fig. 1 is plotted the logarithm of the distillation pressure in cm. as ordinate and the reciprocal of the absolute temperature of boiling as abscissa. The curve on the left is for methyl *iso*propyl hydrazine and that on the right for methyl isopropyl di-imide. The circles were taken from the data of the last two distillations and the cross is the value obtained from the fractional distillation. Since all of these points fall on the same curve, there was no change in the boiling point during the final treatment with aluminum amalgam. The points fall very nearly on a straight line as required by the Clapeyron equation (if A H is assumed

---

[5] Stollé, *J. prakt. Chem.*, [2] **66**, 332 (1902). See also ref. 4.

constant) and by extrapolation the boiling point at 76 cm. pressure is found to be 100.2 ± 0.5°. This boiling point falls between that of symmetrical dimethyl hydrazine (81°) and that of symmetrical di-isopropyl hydrazine (124.5"). The heat of vaporization as given by the slope of the curve of Fig. 1 is found to be 9150 cal. per mole.

This method of preparation should be applicable for other mixed symmetrical hydrazines.



Pig. 1.

Preparation of Methyl Isopropyl **Di-imide.**—Oxidation of the symmetrical methyl *iso*propyl hydrazine by cupric oxide in the presence of a small excess of concd. hydrochloric acid gave a rather poor yield of the azo compound which was probably contaminated by the higher-boiling isomeric hydrazone. Oxidation of the pure symmetrical methyl isopropyl hydrazine with 30% hydrogen peroxide was more successful. The oxidation was carried out on a vacuum line with about 20 cm. of nitrogen at the start. A 50% excess of hydrogen peroxide was added to the symmetrical methyl *iso*propyl hydrazine. The reaction mixture was surrounded by an ice-bath and allowed to remain for half an hour. Then the pressure was gradually reduced and the methyl isopropyl di-imide distilled out of the solution. The gas passed through a tube containing solid sodium bisulfate and calcium chloride, then through a stopcock and was condensed in a tube immersed in an ether–carbon dioxide snow mixture. The stopcock was closed and the liquid evaporated back and forth between two receivers with a calcium chloride tube between them. Non-condensable gases were pumped off several times. Finally the liquid was distilled through a long, upright tube which was cooled with carbon dioxide snow. The gas was allowed to escape very slowly through a stopcock and was condensed in ether-carbon dioxide mixture. The yield was only about

25%. This was due to the rather small quantities prepared and much was lost in the purification process just described.

The purity and boiling point of the liquid were determined from vapor-pressure data. Vapor pressures were determined at three temperatures before distilling one of the samples and then again after distilling about half of the sample. Two-thirds of the sample was collected for experiments on its thermal decomposition. The vapor-pressure data on this sample are plotted on the right part of Fig. 1. The circles represent the first vapor pressures and the crosses the later ones. It is apparent that there was practically no change in the vapor pressures during distillation, which indicates a pure sample. The boiling point was found by extrapolation to be 46.0 ± 0.5'. The heat of vaporization is 7350 cal. per mole.

Due to the explosive nature of aliphatic azo compounds no analysis was made. The identity of the compound was proved by its properties. It has a slight yellow color and its odor is similar to that of dimethyl di-imide. Its boiling point is between that for dimethyl di-imide (1.5') and that for di-isopropyl di-imide (88.5"). The isomeric hydrazone has a higher boiling point (about 90°). The distinguishing properties of azo compounds given by Lochte, Bailey and Noyes[4] are evidently found in this compound. In addition, its thermal decomposition is a very specific test for an azo compound. Preliminary measurements on its decomposition show that methyl isopropyl di-imide decomposes in a homogeneous, unimolecular manner, giving about two moles for each mole of azo compound. It decomposes at about the same rate at 300" as dimethyl di-imide does at 320° and di-isopropyl di-imide at 280". It deviates from the unimolecular rate constant only at pressures below several millimeters. Dimethyl di-imide deviates at pressures below several cm. while di-isopropyl di-imide does not show a reduction in rate even at 0.25 mm. This new mixed azo compound is therefore intermediate in its thermal decomposition.

The completed experiments on the thermal decomposition will be published later.

Summary

Symmetrical methyl isopropyl hydrazine has been prepared by methylating dibenzoyl isopropyl hydrazine with methyl sulfate and hydrolyzing the product in hydrochloric acid solution. The hydrazine derivative is obtained from the acid solution by adding concentrated sodium hydroxide in an atmosphere of nitrogen. It was dried with aluminum amalgam. Methyl isopropyl di-imide was prepared by the oxidation of this hydrazine derivative with hydrogen peroxide. It is a typical azo compound in physical properties and in its thermal decomposition.

STANFORD UNIVERSITY, CALIFORNIA

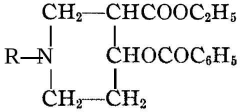
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PIPERIDINE DERIVATIVES. VII. 1-ALKYL-4-PIPERIDYL BENZOATES AND PARA-AMINOBENZOATES[1]

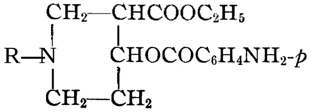
BY N. W. BOLYARD AND S. M. McELVAIN

RECEIVED NOVEMBER 5, 1928 PUBLISHED MARCH 6, 1929

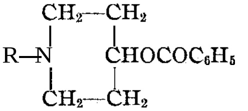
In previous communications[2] two series of piperidine derivatives, the 1-alkyl-3-carbethoxy-4-piperidyl benzoates (I) and the corresponding *p*-aminobenzoates (II) were described These substances are local anesthetics and it was shown that in both series an increase in size of the alkyl group attached to the nitrogen atom caused an increase in the anesthetic activity and a decrease in the toxicity of the compound.



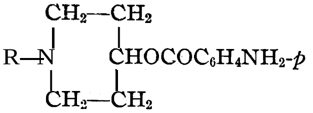
I



II

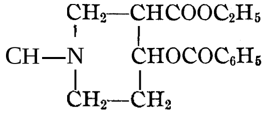


III

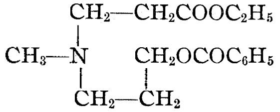


IV

It was desirable, it seemed, to continue the study of this type and to prepare two new series, the 1-alkyl-4-piperidyl benzoates (III) and p-aminobenzoates (IV). These compounds compared as to physiological activity with the former series would show the effect of the presence of the carbethoxy group in the molecule. They would also show whether or not the unusual relationship between the size of the alkyl group attached to the nitrogen and the pharmacological action of the compound that existed in Series I and II could be extended to another series of compounds. Still further relationship between structure and physiological action might be obtained by comparing the first member (where R is methyl) of Series III with 1-methyl-3-carbethoxy-4-piperidyl benzoate (V) and γ-(methyl-β-carbethoxy-ethyl)-aminopropyl benzoate (VI), which have already been described and studied pharmacologically.[3]



V



VI

---

[1] This paper is taken from the thesis submitted by N. W. Bolyard to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

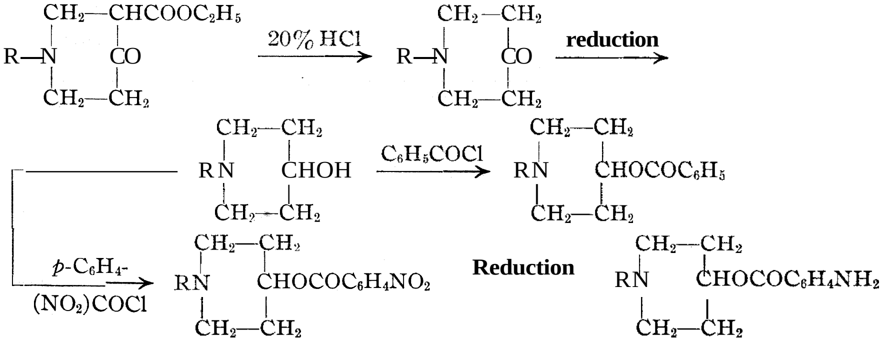
[2] McElvain, THIS JOURNAL, 48, 2179, 2239 (1926).

[3] McElvain, *ibid.*, 46, 1721 (1924).

The pharmacological data indicated that VI was very much less active physiologically than V, from the standpoint of both toxic and anesthetic effects. It was suggested at the time that this difference might be due to the presence of the cyclic structure in V, or to the fact that V contained two points of asymmetry while VI contained none. Consequently it seemed that a pharmacological comparison of these compounds with 1-methyl-4-piperidyl benzoate, in which there is the same cyclic structure that is present in V but no points of asymmetry, would indicate which of these two points of difference was the more fundamental.

In the Series III and IV those compounds in which R is methyl, ethyl, *n*-propyl, *n*-butyl, iso-amyl and phenylethyl have been prepared and submitted for pharmacological study. The phenylethyl derivative was included because it has been found[4] that when this group was attached to the nitrogen in Series II an extremely powerful anesthetic of relatively low toxicity resulted.

These members of Series III and IV were prepared from the corresponding 1-alkyl-3-carbethoxy-4-piperidones.[1] The carbethoxypiperidones were hydrolyzed and decarboxylated by treatment with 20% hydrochloric acid. The 1-alkyl-4-piperidones so obtained were catalytically reduced to the corresponding 4-hydroxypiperidines, which were acylated with benzoyl chloride and *p*-nitrobenzoyl chloride. The *p*-nitrobenzoates were catalytically reduced to the *p*-aminobenzoates. These reactions may be indicated thus



The hydrolysis and decarboxylation of the carbethoxypiperidones took place quite smoothly and yields of 70–92% of the theoretical for the 1-alkyl-4-piperidones were obtained. These piperidones were easily isolated and crystallized as the hydrochlorides. The reduction of these piperidones was carried out using Adams' platinum-oxide platinum black catalyst and proceeded much more rapidly than the reduction of the corresponding carbethoxypiperidones. The latter compounds required about fifty hours for complete reduction, while the 1-alkyl-4-piperidones were

---

[4] Thayer and McElvain, This Journal, 49, 2862 (1927).

completely reduced in six to eight hours. The resulting 1-alkyl-4-hydroxypiperidones were not isolated as such, but were directly acylated and obtained as the hydrochlorides of the benzoates and *p*-nitrobenzoates and as the monohydrochlorides of the p-aminobenzoates.

Experimental

1-Alkyl-3-carbethoxy-4-piperidone Hydrochlorides.—These compounds were prepared by the internal condensation of **β,β'-dicarbethoxydiethylalkylamines** by sodium in xylene.[1] Due to more careful manipulation of the reaction and isolation of the products, yields of 63–78% of the alkyl derivatives, as compared to 50–60% yields originally reported, and 50% yields of the phenylethyl derivative, as compared to a 40% yield reported by Thayer and McElvain, have consistently been obtained.

1-Alkyl-4-piperidone Hydrochlorides.—To 0.1 mole of the 1-alkyl-3-carbethoxy-4-piperidone hydrochloride was added 120 cc. of 20% hydrochloric acid and the resulting solution refluxed for one hour. At the end of this time no coloration was produced in a ferric chloride solution by a drop of the reaction solution. The latter was then evaporated to dryness under diminished pressure and the residue treated with a few small pieces of sodium hydroxide and just enough water to permit the decomposition of the piperidone hydrochloride. The free piperidone was extracted with three 75-cc. portions of ether and the combined extract dried over anhydrous sodium sulfate. The hydrochloride was then precipitated from the ether solution with dry hydrogen chloride and recrystallized from an alcohol–ether mixture. A summary of these piperidones is given in Table I.

TABLE I

1-ALKYL-4-PIPERIDONE HYDROCHLORIDES

1-*Substituent*	Formula	M. p. (corr.), °C.	Yield, %	Analyses, Cl, % Calcd.	Found
Methyl	$C_6H_{12}ONCl$	94– 95	84	23.71	23.25
Ethyl	$C_7H_{14}ONCl$	105–106	70	21.67	21.80
n-Propyl	$C_8H_{16}ONCl$	117–118	70	19.96	i9.67
n-Butyl	$C_9H_{18}ONCl$	178–180	70	18.50	14.62"
Iso-amyl	$C_{10}H_{20}ONCl$	183–185	70	17.24	17.24
Phenylethyl	$C_{13}H_{18}ONCl$	182–184	92	14.79	11.49[a]

[a] The analyses for the *n*-butyl and phenylethyl derivatives gave values for the percentage of chlorine that were considerably lower than the theoretical. Unusual care was exercised in their preparation and purification but no change in the analytical data could be obtained. The sharpness of their melting points suggested that the low analyses might be due to alcohol of crystallization, but drying in *vacuo* at 100° did not cause any change in weight of the material. The benzoyl derivatives obtained from the reduction products of these piperidones showed the calculated halogen content, so it was assumed that the cause of the abnormal halogen content in the case of the piperidones was not fundamental. .

1-Alkyl-4-piperidyl Benzoate Hydrochlorides.—A solution of 10 g. of the 1-alkyl-4-piperidone hydrochloride in 75 cc. of 95% alcohol was shaken with 0.3 g. of Adams' platinum-oxide platinum black catalyst and hydrogen under a pressure of 2–3 atmospheres. The reduction proceeded quite rapidly and at the end of six to eight hours the theoretical amount of hydrogen had been absorbed. The solution was then separated from the catalyst and the alcohol removed under diminished pressure. To the gummy residue which remained 20 cc. of benzoyl chloride was added and the mixture heated in an oil-bath at 150–165° for one hour. When the benzoylation had finished 25 cc.

of absolute alcohol was added to decompose the excess of benzoyl chloride. The resulting alcoholic solution was diluted with 300 cc. of ether and the precipitated hydrochloride of the 1-alkyl-4-piperidyl benzoate allowed to crystallize. These hydrochlorides were recrystallized from an alcohol–ether mixture. They are summarized in Table II.

TABLE II

1-ALKYL-4-PIPERIDYL BENZOATE HYDROCHLORIDES

1-Substituent	Formula	M. p. (corr.), °C.	Yield,[a] %	Analyses, Cl, % Calcd.	Found
Methyl	$C_{13}H_{18}O_2NCl$	219-220	64	13.87	13.75
Ethyl	$C_{14}H_{20}O_2NCl$	204-205	74	13.15	12.73
n-Propyl	$C_{15}H_{22}O_2NCl$	210-211	83	12.50	12.56
n-Butyl	$C_{16}H_{24}O_2NCl$	223-224	73	11.91	12.06
Iso-amyl	$C_{17}H_{26}O_2NCl$	199-200	50	11.38	11.60
Phenylethyl	$C_{20}H_{24}O_2NCl$	236-238	82	10.25	10.17

[a] Recrystallized product based on the piperidone hydrochloride used.

1-Alkyl-4-piperidyl-*p*-nitrobenzoate Hydrochlorides.—These substances were prepared in a manner similar to the benzoates described above except that an equivalent amount of p-nitrobenzoyl chloride was used instead of benzoyl chloride. Acylation took place at a lower temperature (130–145°) in this case. A summary of these p-nitrobenzoate hydrochlorides is given in Table III.

TABLE III

1-ALKYL-4-PIPERIDYL-*p*-NITROBENZOATE HYDROCHLORIDES

1-Substituent	Formula	M. p. (corr.), °C.	Yield, %	Analyses, Cl, % Calcd.	Found
Methyl	$C_{13}H_{17}O_4N_2Cl$	197-199	40	11.79	11.71
Ethyl	$C_{14}H_{19}O_4N_2Cl$	204–206	53	11.27	11.20
n-Propyl	$C_{15}H_{21}O_4N_2Cl$	219-220	48	10.79	11.01
n-Butyl	$C_{16}H_{23}O_4N_2Cl$	242-243	48	10.35	10.30
Iso-Amyl	$C_{17}H_{25}O_4N_2Cl$	243-245	52	9.94	10.15
Phenylethyl	$C_{20}H_{23}O_4N_2Cl$	242-244	55	9.08	9.08

1-Alkyl-4-piperidyl-*p*-aminobenzoate Hydrochlorides.—A solution of 5 g. of the nitrobenzoate hydrochloride in 75 cc. of 95% alcohol was shaken with 0.25 g. of Adams' platinum-oxide platinum black catalyst and hydrogen at 2–3 atmospheres' pressure. The absorption was so rapid that the theoretical amount of hydrogen was taken up in a few minutes. The shaking was continued for one hour to insure complete reduction. The catalyst was then filtered off and the solution evaporated nearly to dryness under diminished pressure. The aminobenzoate was precipitated as the monohydrochloride by the addition of 200 cc. of ether to the concentrated alcoholic solution and it was allowed to crystallize. These hydrochlorides were readily recrystallized from an alcohol–ether mixture. They are summarized in Table IV.

TABLE IV

1-ALKYL-4-PIPERIDYL-*p*-AMINOBENZOATE HYDROCHLORIDES

1-Substituent	Formula	M. p. (corr.), °C.	Yield, %	Analyses, Cl, % Calcd.	Found
Methyl	$C_{13}H_{19}O_2N_2Cl$	231-233	73	13.11	13.47
Ethyl	$C_{14}H_{21}O_2N_2Cl$	183-184	83	12.46	12.50
n-Propyl	$C_{15}H_{23}O_2N_2Cl$	201-203	94	11.87	12.06
n-Butyl	$C_{16}H_{25}O_2N_2Cl$	234-236	82	11.34	11.47
Iso-amyl	$C_{17}H_{27}O_2N_2Cl$	233-235	94	10.86	10.98
Phenylethyl	$C_{20}H_{25}O_2N_2Cl$	238-240	88	9.83	9.82

Pharmacological Report

The 1-alkyl-4-piperidyl benzoates and p-aminobenzoates are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Indianapolis, Indiana. A preliminary report of this work is summarized in Table V. The anesthetic efficiencies were determined in the usual way by application of a 2% solution of the hydrochloride to the rabbit's cornea and noting the duration of anesthesia. Both intravenous and subcutaneous toxicity measurements were made. For comparison the corresponding values that have been obtained for the 1-alkyl-3-carbethoxy-4-piperidyl benzoates and *p*-aminobenzoates with the same 1-substituent are given in parentheses in the table. The data for procaine and cocaine are also included.

TABLE V

PHARMACOLOGICAL DATA

1-Alkyl-4-piperidyl Benzoate Hydrochlorides

		Subcutaneous toxicity to white mice (mg /kg)			Intravenous toxicity to white rats (mg /kg)		
1-Substituent	Av. duration of anesfhesia, min	M. T. D.	M. L. D	No of mice used	M T. D	M. L. D.	No. of rats used
Methyl	27 8 (8)	100 (50)	125 (100)	15 (12)	15	17 5	9
Ethyl	26 6 (0)	250 (100)	300 (150)	26 (15)	20	25	9
n-Propyl	38 (16)	200 (200)	250 (250)	17 (13)	10	12 5	9
n-Butyl	35 5 (29)	100 (1500)	150 (1600)	21 (23)	10	12 5	7
Iso-amyl	34 (40)	600 (4000)	650 (4500)	43 (6)	15	17 5	9
Phenylethyl	202	800	1000	6	20	25	8
I-Alkyl-4-piperidyl *p*-Aminobenzoate Hydrochlorides							
Methyl	4.5 (26)	10 (50)	15 (100)	20 (9)	7 5	10	8
Ethyl	0 (34)	20 (150)	25 (200)	13 (10)	30	35	14
n-Propyl	9 (35)	20 (200)	25 (250)	13 (17)	17.5	20	7
n-Butyl	48 (43)	50 (450)	75 (550)	9 (34)	12.5	15	6
Iso-amyl	58 (72)	75 (500)	100 (550)	32 (25)	10	12.5	11
Phenylethyl	116 (46)	50 (1150)	100 (1200)	12 (40)	10	12.5	10
Cocaine	29	100	150	18	15	17.5	9
Procaine	0	950	1000	20	35	40	15

Discussion of the Pharmacological Data

It will be seen from the data in Table V that the 1-alkyl-4-piperidyl benzoates as a group show a greater anesthetic effect and have very much lower toxicities than the corresponding p-aminobenzoates, while in the series in which there is a 3-carbethoxy substituent in the piperidine nucleus the *p*-aminobenzoyl derivatives show a greater anesthetic effect than the benzoyl derivatives. The carbethoxy group apparently is responsible for this variation in physiological effect.

The 1-alkyl-4-piperidyl benzoates and *p*-aminobenzoates also show the unusual relationship between the size of the alkyl group attached to the nitrogen and toxicity of the compound that was observed in the series containing a 3-carbethoxy substituent. Although the differences are not so great in the new series, it is evident from the data in Table V that in both series an increase in the size of the alkyl group attached to the nitrogen causes an increase in anesthetic effect and a decrease in subcutaneous toxicity.

Particular attention is called to the phenylethyl derivatives, especially 1-phenylethyl-4-piperidylbenzoate. This compound possesses about seven times the anesthetic power of cocaine, a subcutaneous toxicity approximately equal to procaine and an intravenous toxicity intermediate between that of cocaine and procaine. So far as the authors know there is no local anesthetic that approaches this substance in its ability to produce and sustain anesthesia of the rabbit's cornea.

A comparison of the pharmacological data for 1-methyl-3-carbethoxy-4-piperidyl benzoate with those for 1-methyl-4-piperidyl benzoate indicates that there is no apparent connection between the physiological action and the points of asymmetry which are present in the molecule. The latter compound has no asymmetric carbon atoms and is more active than the former which has two such carbon atoms. It would seem, therefore, that one possible explanation that was advanced[3] for the difference in the physiological activity of 1-methyl-3-carbethoxy-4-piperidyl benzoate and γ-(methyl-β-carbethoxy-ethyl)-aminopropyl benzoate (V and VI) was of little or no significance. Such a conclusion, however, is not entirely justified when 1-methyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoate and 1-methyl-4-piperidyl-p-aminobenzoate are considered, for in this case the former with two points of asymmetry is much more active than the latter with no such points of asymmetry. This variation may be due to the presence or absence of the carbethoxy group or to the points of asymmetry in the molecule which the presence of the carbethoxy group causes. The greater the number of different series of compounds that are considered, the more difficult it appears to attribute physiological action to any particular point of structure. Generalizations which fit one series may be quite inapplicable to another. It is probable that the entire molecule functions in producing a certain physiological effect, and what appear to be important structural groupings so modify the effect of each other when they are present in the same molecule that generalizations are extremely difficult, if not impossible.

Summary

1. Two new series of piperidine derivatives, 1-alkyl-4-piperidyl benzoates and *p*-aminobenzoates, have been prepared and described.

2. The members of these series are local anesthetics and show the same relationship between the size of the alkyl group and pharmacological action of the compound as was found to exist in the 1-alkyl-3-carbethoxy-4-piperidyl benzoates and *p*-aminobenzoates.

3. The phenylethyl-4-piperidyl benzoate is a very potent local anesthetic, possessing about seven times the anesthetic power of cocaine and considerably less toxicity.

4. The relationship between physiological action and certain types of structure is discussed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

IMPROVEMENTS IN THE METHOD FOR THE PREPARATION OF MERCURY DIALKYLS FROM ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND ROBERT E. BROWN

RECEIVED NOVEMBER 9, 1928 PUBLISHED MARCH 6, 1929

One of the best methods for the preparation of mercury dialkyls is the reaction between mercuric chloride and the Grignard reagent. Marvel and Gould[1] have described the preparation of several mercury dialkyls by this general reaction. They added the powdered mercuric chloride (about 100 g.) through a condenser in 5- to 10-g. lots over a period of about forty-five minutes and found that a large excess of Grignard reagent and long heating were apparently necessary in order to obtain good yields.

Having a need for large quantities of some mercury dialkyls in connection with studies of magnesium dialkyls, we found that a few variations markedly improved the yields and made the method somewhat more convenient. First, the extra manipulation involved in finely powdering the mercuric chloride and adding it in small portions can be obviated by the use of a Soxhlet extractor. Second, the time of heating was extended from ten to twelve hours to twenty to twenty-four hours. Third, a larger volume of ether was used. These alterations in procedure reduced the tendency of caking and they can be applied to similar reactions involving reactants that are sparingly soluble in ether.

Experimental Part

The reactants were used in the proportions described by Marvel and Gould.[1,2] The Grignard reagent, prepared in 500 cc. of ether, was carefully decanted from the excess magnesium into a two-liter, three-necked flask fitted with an efficient stirrer and a Soxhlet extractor, on top of which was connected a long condenser provided with a drying tube filled with a mixture of calcium chloride and soda lime. The stirrer used was of the

---

[1] Marvel and Gould, THIS JOURNAL, 44, 153 (1922). This article contains a review of earlier work. The authors are indebted to Dr. C. S. Marvel for the suggestion that extended heating would improve the yields. Marvel and Hager, *ibid.*, 48, 2689 (1926) obtained a 90% yield of mercury di-n-heptyl from mercuric chloride and n-heptylmagnesium bromide after a four-day period of refluxing. Marvel and Calvery, ibid., 45,820 (1923), extended the method to the preparation of branched-chain mercury dialkyls.

[2] Although an excess of Grignard reagent is desirable for higher yields, it is possible that the liberal excess used in these experiments can be reduced.

centrifugal type.[3] It consists of a section of glass tube **0.75** inch in diameter and 1.25 inches long with a hole about **0.5** inch in diameter in the center. This is fused opposite the hole onto a glass rod.

The unpowdered mercuric chloride was placed in an extraction thimble and the Grignard reagent was diluted to one liter with anhydrous ether. The flask was warmed by a water-bath until gentle boiling started. The ether solution of mercuric chloride siphoned over into the reaction flask. Care was taken that the ether solution of mercuric chloride did not strike the side of the flask.[4] When all the mercuric chloride had dissolved, usually after about four hours with **100** g. of material, the extractor was removed and the condenser was attached directly to the flask.[5] The temperature of the water-bath was increased to 55–60° and refluxing was continued for an additional eighteen to twenty hours. The reaction mixture was then cooled by an ice-bath and **400** cc. of water was slowly added from a dropping funnel. The ether layer was separated and the water layer was extracted with **50** cc. of ether. After drying the combined ether extracts with calcium chloride, the ether was removed by distillation and the mercury dialkyls fractionally distilled in *vacuo.*

In the following table the time of refluxing includes the four-hour period generally required to extract the mercuric chloride.

TABLE I

MERCURY DIALKYLS

Alkyl bromide	G.	Moles	Magnesium G.	Magnesium Atoms	Mercuric chloride G.	Mercuric chloride Moles	Reflux, hours	Mercury dialkyls, G.	Mercury dialkyls, yield[b] %
Ethyl[a]	125	1.15	30	1.23	97	0.32	22	80	86.5
Ethyl	125	1.15	30	1.23	97	.32	24	82	88.7
Ethyl	250	2.30	60	2.46	194	.64	24	164	88.7
Ethyl	250	2.30	60	2.46	194	.64	24	162	87
n-Butyl[c]	134	0.98	25	1.03	97	.32	16	58.5	52
n-Butyl	134	.98	25	1.03	97	.32	28	75	66.7
n-Butyl	134	.98	25	1.03	97	.32	28	74	66

[a] The mercury diethyl distilled at 65–66° (**18** mm.) uncorrected.

[b] Marvel and Gould (ref. **1**) obtained yields of mercury diethyl ranging from **61** to 75% and their yield of mercury di-n-butyl was 47%. Dr. Marvel has recently carried out some promising experiments on mercury di-n-butyl by first preparing the butyl-mercury halide and then treating this with an excess of Grignard reagent. Also, Mr. Hager obtained excellent yields of mercury di-n-butyl by using a special apparatus for the addition of mercuric chloride. The advantage of the Soxhlet extractor is its general availability.

[c] The mercury di-n-butyl was distilled twice from a Claisen flask provided with a specially indented fractionating side-arm of about **6** inches height to separate the mercury n-butyl halides, of which a considerable quantity was recovered in the distilling flask. The mercury di-n-butyl distilled at 116–118° (**18** mm.). It is probable that the yield of mercury dialkyls can be increased significantly by a more protracted period of refluxing.

---

[3] "The Preparation of Synthetic Organic Chemicals at Rochester," Eastman Kodak Co., see Fig. **21,** p. **26.**

[4] If this solution strikes on or close to the side of the flask, caking may result.

[5] It is probably not necessary to remove the Soxhlet extractor but this was always done. A second condenser may be attached to the other neck of the flask if this is necessary to condense all of the ether vapor.

Summary

Improved directions are given for the preparation of mercury dialkyls from organomagnesium halides.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE]

THE SUPPOSED ALPHA,BETA,BETA-TRIMETHYLGLUTARIC ACID OF NOYES AND SKINNER

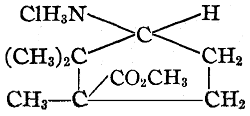
BY FRANCIS EARL RAY

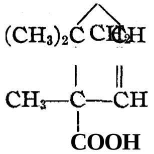
RECEIVED NOVEMBER 15, 1928 PUBLISHED MARCH 6, 1929

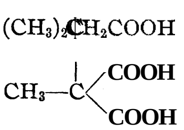
Introduction

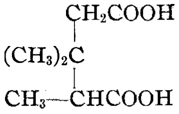
In a previous paper[1] an attempt was made to elucidate the course of the reaction which occurs when the methyl ester of iso-aminocamphonanic acid, I, is decomposed by nitrous acid.

It was thought by Noyes and Skinner[2] that the reaction gave, in part, the unsaturated compound, II, because on oxidation of this product with alkaline permanganate and decomposition with heat, an acid was obtained which was considered to be α,β,β-trimethylglutaric acid, IV.


I


II


III


$$\begin{array}{l} \quad CH_2COOH \\ (CH_3)_2C \\ CH_3{-}CHCOOH \end{array}$$
IV

It was shown[1] that the acid obtained was not α,β,β-trimethylglutaric acid. The suggestion that α,β,γ-trimethylglutaric acid might be formed by the migration of one of the 0-methyl groups was also disproved.

As it then seemed probable that IV was α,α,β-trimethylglutaric acid, Dr. Skinner suggested[3] that a methyl group might migrate from the β- to the a-position when carbon dioxide is liberated by heat from III. It is this possibility with which the present investigation deals.

Discussion

Perkin and Thorpe[4] had obtained α,β,β-trimethylglutaric acid by decomposing the ethyl ester of α,β,β-trimethyl-α-cyanoglutaric acid with hydrochloric acid in a sealed tube at 200° without isolating the intermediate α,β,β-trimethyl-α-carboxyglutaric acid. It seemed possible that this vigorous treatment might prevent a migration that would take place under the influence of heat alone.

---

[1] Ray, THIS JOURNAL, 50, 558 (1928).

[2] Noyes and Skinner, *ibid.*, 39, 2692 (1917).

[3] Private communication.

[4] Perkin and Thorpe, J. *Chem.* Soc., 75, 65 (1899).

Accordingly, the a,β,β-trimethyl-α-carboxyglutaric acid was prepared after many attempts and decomposed by heat. It gave, however, the α,β,β-trimethylglutaric acid, showing no evidence of the migration of a methyl group.

An examination of Dr. Skinner's analytical data[2] for the tricarboxylic acid shows that they correspond to an acid of molecular weight 193 or 194. As trimethylcarboxyglutaric acid has a molecular weight of 218, the explanation of the reaction was based on an error in the interpretation of the analytical data.

The analytical data of Noyes and Skinner seem to indicate that their tribasic acid was a carboxydimethylsuccinic acid, but the melting point of their dibasic acid does not correspond to the melting point of either the unsymmetrical or the fumaroid or maleinoid form of the symmetrical dimethylsuccinic acid. The nature of their acid, and of the unsaturated isomer of lauronolic acid from which it was obtained, must be considered uncertain.

Experimental Part

Diethylacrylic Ester.—This ester was prepared from *iso*-amyl alcohol by oxidation with dichromate, bromination, esterification and removal of hydrobromic acid by boiling with quinoline; b. p. 60–65" (5 mm.).

β,β-Dimethyl-α-cyanoglutaric Ester.—Fifty-four g. of dimethylacrylic ester, 60 g. of cyanoacetic ester, 12 g. of sodium and 200 cc. of absolute alcohol dried with magnesium methylate were boiled for fifteen hours; 75 g. of methyl iodide was added and the mixture heated for five hours. In other experiments the mixture with methyl iodide was heated in a pressure flask from six to twenty-four hours. On saponification with potash and decomposition an acid was obtained that melted at 99–100°.[5] The analysis showed that the third methyl group did not enter the molecule.

Anal. Subs., 0.2002: H_2O, 0.1364; CO_2, 0.3853. Calcd. for $C_7H_{12}O_4$: H, 7.50; C, 52.50. Found: H, 7.62; C, 52.49.

This difficulty was finally overcome by methylating in an'alcohol-free ether or in a benzene solution.

α,β,β-Trimethyl-α-carboxyglutaric Acid.—This acid was not isolated by Perkin and Thorpe.[4] They obtained only compounds containing nitrogen on heating the ester with potash. In a previous paper[1] it was shown that prolonged boiling with strong potash is necessary to obtain the acids from these esters. In this case, after boiling the ester for twenty hours with 50% potash, the solution was evaporated to dryness and heated to 120° for ten hours. The dry salt was washed with ether, dissolved in water, acidified and extracted with ether. On spontaneous evaporation of the ether the mass crystallized. It was recrystallized, first from hydrochloric acid and then from benzene. After nine recrystallizations it melted at 189–190° with evolution of carbon dioxide.

After heating for thirty minutes at 200°, the mass was recrystallized four times from benzene; m. p. 86°. Perkin and Thorpe[4] give 86–87° for α,β,β-trimethylglutaric acid.

Anal. Subs., 0.0587: Ag, 0.0325. Calcd. for $Ag_2C_8H_{12}O_4$: Ag, 55.64. Found: Ag, 55.40.

---

[5] Perkin and Goodwin give 101° for β,β-dimethylglutaric acid, *J. Chem. Soc.*, ***60***, 1472 (1896).

The writer expresses his thanks to Professor W. A. Noyes for advice and help during the progress of this investigation.

Summary

The explanation given by Noyes and Skinner for the formation of the unsaturated acid obtained by the decomposition of iso-aminocamphonanic acid with nitrous acid is shown to be based on an erroneous interpretation of the analytical data.

No member of the trimethylglutaric acid series is formed on oxidation of this unsaturated acid.

The decomposition of α,β,β-trimethyl-α-carboxyglutaric acid proceeds normally, giving α,β,β-trimethylglutaric acid whether decomposition is effected by heat alone or by heating the ester with hydrochloric acid in a sealed tube at 200".

GRINNELL, IOWA

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

SYMMETRICAL DIPHENYL-TETRA-TERTIARY-BUTYLETHYNYLETHANE

BY S. S. ROSSANDER AND C. S. MARVEL

RECEIVED NOVEMBER 16, 1928 PUBLISHED MARCH 6, 1929

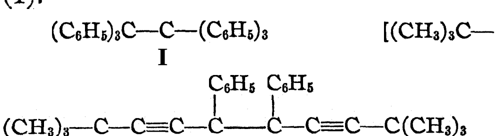
As the first step in a study of the effect of acetylenic groups on the stability of the ethane linkage in a hexa-substituted ethane, Salzberg and Marvel[1] have prepared hexa-*tert.*-butylethynylethane (II). This hydrocarbon was found to be stable toward oxygen and in this respect to differ very markedly from the hexa-aryl ethanes. However, it did react with 1% sodium amalgam to give tri-*tert.*-butylethynylmethyl sodium. This reaction indicates that this hexa-substituted ethane has a central linkage that is about as easily ruptured with metals as that in hexaphenylethane (I).

$(C_6H_5)_3C-C-(C_6H_5)_3$

I

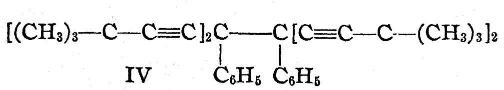
$[(CH_3)_3C-C\equiv C]_3C-C[C\equiv C-C-(CH_3)_3]_3$

II



$$(CH_3)_3-C-C\equiv C-\underset{C_6H_5}{\overset{C_6H_5}{C}}-\underset{C_6H_5}{\overset{C_6H_5}{C}}-C\equiv C-C(CH_3)_3$$

III



$$[(CH_3)_3-C-C\equiv C]_2\underset{C_6H_5}{C}-\underset{C_6H_5}{C}[C\equiv C-C-(CH_3)_3]_2$$

IV

For further information concerning these acetylenic derivatives a study of the compounds intermediate between hexaphenylethane and hexa-*tert.*-butylethynylethane has been made. **A** hydrocarbon $C_{38}H_{38}$, which may be *sym.*-tetraphenyl-di-*tert.*-butylethynylethane (III), was described

---

[1] Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928).

by Salzberg and Marvel.[2] This hydrocarbon was much more stable than was expected for one with the structure represented by Formula III.

In the present paper the preparation and properties of *sym.*-diphenyl-tetra-*tert.*-butylethynylethane (IV) are described. This hydrocarbon was produced by the action of silver on phenyl-di-*tert.*-butylethynylbromomethane. It is stable in oxygen and shows no tendency to form a peroxide. When a solution is heated, color develops and this color does not disappear when the solution is cooled. It is changed by heat but apparently does not rearrange to a solid stable compound as does hexa-*tert.*-butylethynylethane. It reacts with 40% sodium amalgam and with liquid sodium–potassium alloy to give the alkali metal derivative of phenyl-di-*tert.*-butylethynylmethyl. It does not react with 1% sodium amalgam.

There is little doubt concerning the structure of this hydrocarbon, since the alkali metal derivatives obtained by splitting the ethane can be converted into phenyl-di-*tert.*-butylethynylacetic acid. For comparison this acid was prepared from phenyl-di-*tert.*-butylethynylbromomethane by the Grignard reaction.

If the reaction between silver and phenyl-di-*tert.*-butylethynylmethyl bromide is carried out in the presence of oxygen, the ethane is not produced. Instead, oxygen is absorbed and only tarry products are left when the solvent is removed. The amount of oxygen absorbed is greater than would be needed for the formation of a peroxide. This absorption of oxygen is similar to that observed in the cask of diphenyl-*tert.*-butylethynylbromomethane. It is especially interesting in this connection to note that in the reaction of tri-*tert.*-butylethynylbromomethane with silver no oxygen is absorbed.

Experimental Part

Phenyl-di-*tert.*-butylethynylcarbinol.—The Grignard reagent was prepared from 20 g. of *tert.*-butylacetylene by adding it from a separatory funnel to 75 cc. of a 4.116 N ether solution of ethylmagnesium bromide. The heat of the reaction caused the ether to reflux and an efficient condenser filled with water at about 5° was needed to avoid loss of the acetylene. To the ether solution of the Grignard reagent was added 23 8 g. of ethyl benzoate. The best results were obtained by adding half of the ester, stirring for three or four hours and then adding the second half of the ester over a period of two hours. The mixture was stirred for two hours longer and then it was decomposed by pouring into an ice-cold solution of saturated ammonium chloride. The ether layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue was distilled under reduced pressure. The product boiled at 135–139° (1.5 mm.). This product solidified after standing at 0° for about ten days. The material was recrystallized by dissolving in petroleum ether and cooling the solution in carbon dioxide snow. The yield of recrystallized carbinol was 10–12 g. (55–64% of the theoretical amount); m. p. 46–47°.

Anal. Subs., 0.2182: CO_2, 0.6788; H_2O, 0.1745. Calcd. for $C_{19}H_{24}O$: C, 85.02; H, 9.03. Found: C, 84.84; H, 8.96.

---

[2] Salzberg and Marvel, THIS JOURNAL, 50,2840 (1928).

This carbinol was rearranged to the α,β-unsaturated ketone by dissolving 1 g. in 6 cc. of glacial acetic acid and adding to the solution 1 cc. of concentrated sulfuric acid. The mixture was poured into cracked ice and the ketone was extracted with ether. The ether was concentrated to about 10 cc. and cooled in carbon dioxide snow. The ketone was separated as yellow crystals. After four recrystallizations a product was obtained which melted at 108–110°. An ether solution of this product did not react with sodium. The yield was only 0.5 g.

Anal. Subs., 0.1074: CO_2, 0.3346; H_2O, 0.0865. Calcd. for $C_{19}H_{24}O$: C, 85.02; H, 9.03. Pound: C, 84.96; H, 9.00.

Phenyl-di-*tert*.-butylethynylbromomethane.—Three g. of the carbinol was dissolved in 20 cc. of dry ether and the solution was cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution was stirred at 0° for one-half hour. To the mixture was added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The ether layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The residue was dissolved in the least possible amount of absolute ether and 8 cc. of absolute alcohol was added. This solution was again evaporated under reduced pressure until crystals appeared and was then allowed to stand at about 0° overnight until the bromo compound had crystallized. It was collected on a filter and then again crystallized from ether and alcohol. After drying in a vacuum desiccator there was obtained 2.4 g. (60% of the theoretical amount) of a white crystalline product; m. p. 58–59°.

Anal. Subs., 0.2431: CO_2, 0.6152; H_2O, 0.1502. Subs., 0.2011: 3.9cc.of0.1540 N $AgNO_3$. Calcd. for $C_{19}H_{23}Br$; C, 68.85; H, 6.99; Br, 24.13. Found: C, 69.00; H, 6.91; Br, 24.15.

The filtrates from this bromo compound were evaporated to dryness and the residue was heated with acetone and then recrystallized. A few colorless crystals melting at 169–174° were obtained. The product contained bromine but not enough material was isolated for further identification.

***Sym*.-diphenyl-tetra-*tert*.-butylethynylethane.**—A solution of 2.048 g. of phenyl-di-*tert*.-butylethynylbromomethane in 10 cc. of absolute ether was shaken with 2 g. of molecular silver for twenty-four hours. The solution was filtered and evaporated under reduced pressure almost to dryness. To the residue was added 8 cc. of absolute alcohol and the evaporation was continued until crystals began to form. The mixture was cooled to 0° for a few hours and filtered. The yield of hydrocarbon was 0.75–0.9 g. (40–50% of the theoretical amount). After recrystallization from ether and alcohol it melted at 98–99°.

Anal. Subs., 0.2010: CO_2, 0.6700; H_2O, 0.1670. Calcd. for $C_{38}H_{46}$: C, 90.85; H, 9.24. Found: C, 90.91; H, 9.22.

A solution of 0.4 g. of the ethane in 15 cc. of bromobenzene at about 100° was shaken in an atmosphere of oxygen for six hours. No absorption of oxygen was observed. The solution did turn yellow at 100° but the color did not disappear on cooling.

Effect of Heat on the Hydrocarbon.—A solution of 0.2 g. of the ethane in 4 cc. of hexane was heated in a sealed tube at 100° for one hour. The solution became light yellow and the color remained when the solution was cooled.

A solution of 0.22 g. of the ethane in 4 cc. of absolute alcohol was heated in a sealed tube to 100° for one hour. The solution became intensely yellow. The color did not disappear on cooling. On working up the solution 0.14 g. of the ethane was recovered.

A solution of 0.4 g. of the ethane in 15 cc. of xylene was refluxed gently for one hour. The solution turned dark red in color. When the solution was evaporated and the residue crystallized from alcohol and ether, 0.19 g. of the ethane was recovered. There was some oily residue which did not crystallize. A solution of 0.2 g. of the ethane in xylene was heated in a sealed tube to 140° for one hour. The color was yellow when air was thus excluded. From this reaction 0.1 g. of the ethane was recovered.

Cleavage of the Ethane with Alkali Metals,—A solution of 0.55 g. of the ethane in 10 cc. of dry ether was shaken with 5 cc. of liquid sodium–potassium alloy in an atmosphere of *dry* nitrogen. The solution turned red in about thirty seconds and was very deeply colored in one and one-half minutes. After twenty-four hours an excess of moist carbon dioxide was passed in until the solution became clear. The mixture was heated with 50 cc. of water containing 5 g. of potassium hydroxide. The mixture was heated to evaporate the ether and then cooled and filtered. The solution was cooled to 0°, acidified with dilute hydrochloric acid and a white precipitate of organic acid separated. After repeated crystallization from petroleum ether and methyl alcohol (using Norite to decolorize each solution), there was obtained a small amount of acid, m. p. 154-156". This was found to be identical with phenyl-di-*tert.*-butylethynylacetic acid described below.

A solution of 1 g. of the ethane in 10 cc. of dry ether was shaken with 8 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen. After about twenty seconds the surface of the alloy was tinged with red and the solution was yellow. After about eighty seconds the solution turned red. After shaking for twenty hours the mixture was decomposed with moist carbon dioxide and the acid isolated as described above. The yield of crude acid, which was still yellow in color, was 0.73 g. (56% of the theoretical amount). The recrystallized material melted at 154–156°. In the crystallization it was found that much of the yellow color was absorbed on the filter paper on allowing the crude material to stand in a funnel.

Anal. Subs., 0.2031: CO_2, 0.6040; H_2O, 0.1467. Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.17. Found: C, 81.11; H, 8.08. *Neutral equivalent.* Subs., 0.1025: 2.85 cc. of 0.1215 N NaOH. Calcd. for $C_{20}H_{24}O_2$: 296.2. Found: 293.4.

When a solution of 0.1 g. of the ethane in 10 cc. of ether was shaken with 3 cc. of 1% sodium amalgam in an atmosphere of dry nitrogen for three days, no color was developed. Practically all of the ethane (0.082 g.) was recovered on evaporation and crystallization of the residue.

Phenyl-di-*tert.*-butylethynylacetic acid.—To prove the structure of the acid obtained by splitting the ethane with alkali metals, phenyl-di-*tert.*-butylethynylacetic acid was prepared from phenyl-di-*tert.*-butylethynylbromomethane. This was accomplished by the action of 40% sodium amalgam on the bromide to give the sodium derivative of phenyl-di-*tert.*-butylethynylmethyl which, with carbon dioxide, gave the acid and also by the action of magnesium and carbon dioxide on the bromide.

A solution of 1 g. of phenyl-di-*tert.*-butylethynylbromomethane in 10 cc. of dry ether was shaken with 4 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen for twenty-four hours. The solution was then treated with moist carbon dioxide as described under the splitting of the ethane. The acid was isolated as before and the yield was 0.6 g. (66% of the theoretical amount). This product after several recrystallizations from petroleum ether and methyl alcohol melted at 154–156° and showed no depression in melting point when mixed with the acids obtained by splitting the ethane with sodium–potassium alloy or 40% sodium amalgam.

Anal. Subs., 0.1890: CO_2, 0.5606; H_2O, 0.1344. Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.17. Found: C, 81.05; H, 7.95. *Neutral equivalent.* Subs., 0.1006: 2.8 cc. of 0.1215 N NaOH. Calcd. for $C_{20}H_{24}O_2$: 296.2. Found: 295.0.

The same acid was obtained by the action of carbon dioxide and magnesium on the bromide. To a solution of 2 g. of phenyl-di-*tert.*-butylethynylbromomethane in 10 cc. of dry ether was added 0.15 g. of magnesium and about 0.01 g. of iodine. The mixture was stirred and a slow current of dry carbon dioxide was passed over the surface of the ether. More ether was added from time to time as it evaporated. After about five hours the mixture was decomposed with dilute hydrochloric acid and the organic acid was extracted from the ether with a solution of 5 g. of sodium hydroxide in 50 cc. of water. The acid was reprecipitated and the yield of crude acid was about 1 g. After recrystallization it melted at 154–156° and showed no depression in the melting point when mixed with the acid prepared from the ethane by splitting with alkali metals and treating with carbon dioxide.

When an attempt was made to prepare the Grignard reagent from the bromide first, and then to convert it to the acid by the action of carbon dioxide, only the ethane was obtained.

Reaction of Phenyl-di-*tert.*-butylethynylbromomethane and Silver in an Atmosphere of Oxygen.—A solution of 0.5 g. of the bromide in 5 cc. of ether was treated with 0.5 g. of molecular silver in an atmosphere of dry oxygen. The reaction mixture was shaken by hand from time to time. In about ten hours the reaction mixture had absorbed the theoretical amount of oxygen (18.4 cc. at 25° and 745 mm.) for the formation of a peroxide. In twelve hours a total of 25.5 cc. of oxygen was absorbed. No further absorption occurred in four hours more. The solution was evaporated under reduced pressure but only oily products were obtained.

Another run of 0.2 g. of the bromide was made and the reaction was discontinued when the theoretical amount of oxygen had been taken up by the reaction mixture. No crystalline products were isolated on evaporation of the solution.

Summary

1. *Sym.*-di-phenyl-tetra-*tert.*-butylethynylethane has been obtained by the action of silver on phenyl-di-*tert.*-butylethynylbromomethane.

2. The hydrocarbon reacts with 40% sodium amalgam or with liquid sodium–potassium alloy to give the alkali metal derivative of phenyl-di-*tert.*-butylethynylmethyl. The ethane does not react with 1% sodium amalgam.

3. The properties of this hydrocarbon are intermediate between those of hexa-*tert.*-butylethynylethane and of the hydrocarbon $C_{38}H_{38}$ obtained by the action of silver on diphenyl-*tert.*-butylethynylbromomethane.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED ACIDS

BY GEORGE H. COLEMAN AND GEORGE M. MULLINS[1]

RECEIVED NOVEMBER 17, 1928 PUBLISHED MARCH 6, 1929

The addition of nitrogen trichloride to unsaturated hydrocarbons,[2] unsaturated ketones,[3] and diphenylketone[4] has been reported previously.

Nitrogen trichloride also reacts with unsaturated acids to form small yields of stable addition products and large amounts of nitrogen and chlorine. The chlorine is taken up in part by the excess of unsaturated acid present. Very small amounts of ammonium chloride are formed and in this respect the reaction differs from most of the other reactions of nitrogen trichloride with unsaturated compounds.

The reaction was studied with crotonic acid and cinnamic acid. With crotonic acid the α-chloro-β-dichloro-aminobutyric acid first formed is converted by the hydrochloric acid produced in the solution to β-amino-α-chlorobutyric acid, which precipitates slowly from the carbon tetrachloride solution as the hydrochloride. A similar precipitation of the hydrochloride has been observed with benzalacetone,[3b] methylpropene[2b] and toluene,[5] although this is not characteristic of many of the reactions of nitrogen trichloride with unsaturated compounds. At 20° ten days or longer is required for the complete precipitation of the hydrochloride. It seems probable, however, that the primary addition takes place more rapidly than this. At lower temperatures a longer time is required for the completion of the reaction, but the yields are better and the product slightly purer. The free aminochloro acid was prepared from the hydrochloride and its structure established by reduction to β-aminobutyric acid.

In the case of cinnamic acid the limited solubility of the compound in carbon tetrachloride made it necessary to use a suspension of the finely powdered acid and required the separation of the product from the excess cinnamic acid. Carbon tetrachloride is probably the best solvent for use with nitrogen trichloride, particularly when the reaction mixture is to stand several days. The reaction rate of cinnamic acid is not far different from that of crotonic acid. The dichloro-amino group again enters the β-position. The structure of the product was established by reduction to β-amino-β-phenylpropionic acid.

---

[1] This paper is an abstract of a part of the thesis submitted by George M. Mullins in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

[2] (a) Coleman and Howells, THIS JOURNAL, 45, 3084 (1923); (b) Coleman, Mullins and Pickering, *ibid.*, 50, 2739 (1928).

[3] (a) Coleman and Craig, *ibid.*, 49, 2593 (1927); (b) 50, 1816 (1928).

[4] Coleman and Campbell, *ibid.*, 50, 2754 (1928).

[5] Coleman and Noyes, *ibid.*, 43, 2211 (1921).

Experimental

The Reaction of the Crotonic Acid

The Preparation of the Hydrochloride of β-Amino-α-chlorobutyric Acid.—Nitrogen trichloride was prepared and analyzed as described in previous papers.[2b] Solutions containing about 1.5 mg. moles of nitrogen trichloride per gram of solution were used. The crotonic acid was dissolved in enough carbon tetrachloride for complete solution, the nitrogen trichloride was added and the apparatus arranged for collecting the gas evolved. Eighteen runs were made using varying proportions of crotonic acid and nitrogen trichloride and carrying out the reaction at different temperatures. It was found that about 1.5 moles of crotonic acid was required for each mole of nitrogen trichloride. Very little increase in yield was observed when a larger excess of acid was used. In the following table several representative yields obtained at different temperatures are given. For each mole of nitrogen trichloride 1.5 moles or more of crotonic acid was used.

TABLE I

PERCENTAGE YIELDS OF β-AMINO-α-CHLOROBUTYRIC ACID PROM NITROGEN TRICHLORIDE AND CROTONIC ACID

Yields at 0°, %	14.6	9.3	14.6
Yields at 13°, %	18.4	16.4	19.7
Yields at 20°, %	10.5	13.1	12.8

The solutions remained clear for a short time after mixing but soon became opalescent and a slow precipitation of the hydrochloride of the aminochloro acid continued for some days. At 20" ten days or longer was required for complete precipitation. The rate of evolution of nitrogen indicated, however, that the primary reaction was more rapid than this. At the lower temperatures a longer time was required. The product obtained at 0 and 13° was soluble in absolute ethyl alcohol and analysis indicated that it was the hydrochloride with only traces of impurities. The reaction product at 20° contained a small amount of ammonium chloride. For analysis the slightly impure product was purified by dissolving in absolute n-propyl alcohol, filtering and reprecipitating with anhydrous ether. If necessary this was repeated.

Anal. Subs., 0.1355, 0.1285: 15.38, 15.03 cc. of 0.1008 *N* $AgNO_3$. Subs., 0.0629, 0.0126: 35.75, 7.21 cc. of 0.01 N HCl. Calcd. for $C_4H_9O_2NCl_2$: Cl, 40.80; N, 8.05. Found: Cl, 40.61, 40.75; N, 7.96, 8.01.

β-Amino-α-chlorobutyric Acid.—The free aminochloro acid was prepared by dissolving the hydrochloride in absolute methyl, ethyl or n-propyl alcohol and adding pyridine[6] or by adding the calculated amount of lithium hydroxide to an aqueous solution of the hydrochloride, evaporating until crystals formed and adding ten volumes of alcohol.[7] The highest yields obtained by each method were as follows: CH_3OH and C_5H_5N, 63%; C_2H_5OH and C_5H_5N, 70%; C_3H_7OH and C_5H_5N, 80%; LiOH and C_2H_5-OH, 60%. After several recrystallizations from 80% ethyl alcohol, the acid was obtained as white needles melting at 161–161.5° (uncorr.).

Anal. Subs., 0.1229, 0.1673: 8.61, 11.85 cc. of 0.1032 N $AgNO_3$. Subs., 0.3818, 0.0905: 28.32, 6.88 cc. of 0.0964 *N* HCI. Calcd. for $C_4H_8O_2NCl$: Cl, 25.82, N, 10.18, Found: Cl, 25.66, 25.95; N, 10.00, 10.25.

Benzoyl-β-amino-α-chlorobutyric Acid--0.3 g. of the purified hydrochloride was dissolved in 10 cc. of water, three times the theoretical amount of benzoyl chloride

---

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, 4, 31 (1924).

[7] Fischer and Raske, *Ber.*, 40, 3720 (1907).

and 5 cc. of a 45% solution of sodium hydroxide were added and the mixture was thoroughly shaken. After several hours the solution was acidified and the precipitate filtered off and dried. When the precipitate was thoroughly dry the benzoic acid was removed by repeated extraction with boiling petroleum ether (b. p. 120–140°). After several recrystallizations from water the product melted at 174–174.5° (uncorr.).

β-Aminobutyric Acid.—Several attempts were made to reduce the aminochloro acid to the amino acid with sodium amalgam in both acid and alkaline aqueous solution at room temperature and at 0°. The chlorine was not completely removed. The reduction was finally carried out in an alkaline methyl alcohol solution. The hydrochloride was dissolved in about 20 times its weight of methyl alcohol and several times the theoretical amount of sodium amalgam (2.5%) added very slowly with constant stirring. When the reaction was complete the alcohol was evaporated on a water-bath. The residue was taken up with water and concentrated hydrochloric acid added. The solution was evaporated to dryness as before and the residue extracted with n-propyl alcohol. Pyridine was then added and the product thus obtained was recrystallized from 80% ethyl alcohol. After several recrystallizations the compound melted at 184–185° (uncorr). The melting point recorded for β-aminobutyric acid is 184° and that for α-aminobutyric acid 292° (decomp.). The product gave no test for chlorine by the Beilstein method.

Anal. Subs., 0.0167, 0.0204: 16.07, 19.51 cc. of 0.01 N HCl. Calcd. for $C_4H_9O_2N$: N, 13.59. Found: N, 13.50, 13.39.

The Reaction with Cinnamic Acid

Preparation of the Hydrochloride of β-Amino-α-chloro-β-phenylpropionic Acid.—The reaction with cinnamic acid was carried out in much the same manner as that with crotonic acid. The limited solubility of cinnamic acid in carbon tetrachloride made it necessary to use the acid partly dissolved and partly suspended in finely powdered form in the solution. The reaction mixtures were allowed to remain at room temperature for two weeks. Dry hydrogen chloride was then passed into the solution and the product, together with some unchanged cinnamic acid, was filtered off. This was shaken several times with anhydrous ether to free it from the cinnamic acid. The yields of crude product varied from 5 to 8.5%, calculated from the nitrogen trichloride.

The crude hydrochloride was purified by a method similar to that used by Posner[8] with β-phenylalanine. The crude product was treated with a little concentrated hydrochloric acid and the mixture evaporated to dryness on a water-bath. The residue was taken up with methyl alcohol, the solution decolorized with charcoal and the hydrochloride reprecipitated by the addition of five volumes of ether. The product melted at 228–230° (uncorr.).

Anal. Subs., 0.1365, 0.1706: 5.86, 7.35 cc. of 0.0983 N HCl. Subs., 0.2037, 0.1422: 17.07, 11.94 cc. of 0.1008 N $AgNO_3$. Calcd. for $C_9H_{11}O_2NCl_2$: N, 5.93; Cl, 30.08. Found: N, 5.91, 5.85; Cl, 29.99, 30.05.

β-Amino-α-chloro-β-phenylpropionic Acid.—The free aminochloro acid was prepared by dissolving 0.77 g. of the hydrochloride in 15 cc. of methyl alcohol and adding 4 cc. of pyridine; 0.40 g. of white precipitate formed on standing. After recrystallizing from 80% ethyl alcohol, the product melted at 199–200° (uncorr.).

Anal. Subs., 0.0202, 0.0514: 10.10, 25.63 cc. of 0.01 N HCl. Subs., 0.1157, 0.0551: 5.70, 2.73 cc. of 0.1008 N $AgNO_3$. Calcd for $C_9H_{10}O_2NCl$: N, 7.01; Cl, 17.79. Found: N, 7.00, 6.98; Cl, 17.60, 17.69.

Benzoyl-β-amino-β-phenylpropionic Acid.—The hydrochloride of the aminochloro

---

[8] Posner, *Ber.*, 38, 2321 (1905).

acid was dissolved in a small amount of water and six times the theoretical amount of sodium amalgam added very slowly with constant stirring. When the reaction was complete the solution was acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residue was taken up with methyl alcohol, the solution filtered and evaporated as before. The product was weighed and the calculated amount of 0.1 N sodium hydroxide added to free the acid from the hydrochloride. This was evaporated until crystals began to form and then allowed to stand at 0° for twenty-four hours. This method was used since β-amino-β-phenylpropionic acid is soluble in alcohol and the methods used for the other acids were not applicable. A 65% yield of crude product was obtained which contained no chlorine. The melting point was, however, too low and the compound could not be readily purified. The benzoyl derivative was prepared as described for β-amino-α-chlorobutyric acid. The melting point of the purified product was 194–195° (uncorr.). A mixed melting point was taken with the known compound prepared by another method.

Anal. Subs., 0.0200, 0.0201: 7.65, 7.66 cc. of 0.01 N HCl. Calcd. for $C_{16}H_{15}O_3N$: N, 5.21. Found: N, 5.36, 5.34.

Summary

Nitrogen trichloride reacts with crotonic acid to form, among other products, α-chloro-β-dichloro-aminobutyric acid, which is changed by hydrochloric acid to β-amino-α-chlorobutyric acid. The structure of the compound was established by reduction to the corresponding amino acid.

A similar reaction occurs with cinnamic acid. The dichloro-amino group again enters the 8-position.

IOWA CITY, IOWA

[Contribution from the Chemical Laboratory of Bryn Mawr College]

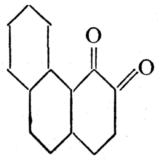
SOME DERIVATIVES OF 3,4-PHENANTHRENEQUINONE

By Louis Frederick Fieser

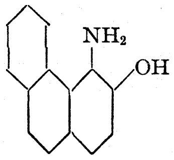
Received November 17, 1928 Published March 6, 1929

In the belief that a knowledge of the reduction potentials of ortho- or para-quinones derived from phenanthrene, but isomeric with 9,10-phenanthrenequinone, would throw some additional light on the general problem of the relationship between the oxidizing power and the structure of the various quinones, the author undertook to prepare one or two compounds of the isophenanthrenequinone type, and to compare them, by the potentiometric method, with the corresponding naphthoquinones. In the course of this work it soon became evident that the isophenanthrenequinones, which have received scarcely any attention up to the present time, are interesting from several points of view other than that of the original problem, and the work has thus developed into a rather extensive study of the general chemistry and the methods of obtaining various isophenanthrenequinones and compounds derived from them. The presentation of the results of investigations which are concerned solely with the chemistry of phenanthrene derivatives will be followed with an account of the electrochemical data which have accumulated.

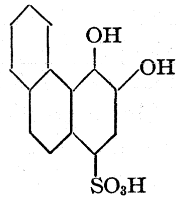
3,4-Phenanthrenequinone (I).—This is the only one of the isophenanthrenequinones of the type indicated which has been described up to the present time. Barger[1] obtained the quinone by oxidizing morphol with silver oxide; the morphol which he employed was prepared by converting 3-phenanthrol into an ortho-aldehyde and oxidizing the latter substance with hydrogen peroxide, A more convenient method was suggested by an unexplained observation of Werner and his students.[2] These investigators, in the course of a careful study of 3-phenanthrol, converted this compound into an amino-3-phenanthrol by coupling with a diazonium salt and reducing the azo dye. When they attempted to diazotize the amino-3-phenanthrol hydrochloride, as the first step in the proposed conversion of the compound into a dihydroxyphenanthrene, they were surprised to find that nitrous acid converted the salt into a sparingly soluble, easily decomposed, yellow substance. Since the substance was obviously not a diazonium salt, their original plan was abandoned, though it is now clear that they were very close to achieving one of the aims of the extensive studies on phenanthrene undertaken by Werner, namely, the preparation of morphol from the hydrocarbon. It appeared probable to the author that the colored substance was a quinone, produced by the oxidizing action of nitrous acid, and investigation has shown that this is the case and that the substance is 3,4-phenanthrenequinone. On reduction it yields morphol, while morpholquinone may be obtained from it by known methods. It is thus clear that 3-phenanthrol couples in the 4-position and that the amine has the structure of II.



I



II



III

It has been found possible to carry out the preparation of 4-amino-3-phenanthrol hydrochloride on a large scale in a simple manner. The dyestuff formed on interaction with diazotized sulfanilic acid is reduced, without being isolated, by means of sodium hyposulfite. The oxidation of the amine hydrochloride is best accomplished by adding an aqueous solution of chromic acid to a suspension of the salt in glacial acetic acid. The yields in all of these reactions are good.

3,4-Phenanthrenequinone is characterized by the brilliant red color of its crystals and by a beautiful color reaction with concentrated sulfuric acid. Though certain precautions must be observed in order to prevent

Barger, *J. Chem. Soc.*, 113,218 (1918).

Werner, Löwenstein, Wack and Kunz, Ann., 321,297 (1902).

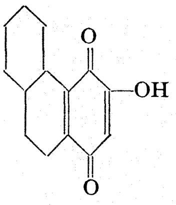
the destruction of a considerable quantity of the material during the course of its preparation, the pure quinone is a quite stable substance. Like other ortho-quinones it adds a molecule of sodium bisulfite with the formation of a sulfonic acid derivative of the hydroquinone. In consideration of the nature of this reaction, the substance must have the structure of 3,4-dihydroxy-phenanthrene-1-sulfonicacid, III, and this is confirmed by the conversion of the substance into the para-quinone described below. The sulfonic acid was isolated in the form of the *p*-toluidine salt and was converted into the corresponding quinone by oxidation.

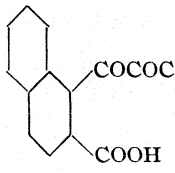
3-Hydroxy-1,4-phenanthrenequinone.—A fairly satisfactory method of preparing this compound, which is the first representative 1,4-phenanthrenequinone to be described, was found in the oxidation of 3,4-dihydroxyphenanthrene-1-sulfonic acid in alkaline solution with hydrogen peroxide. The quinone separates in the form of a sparingly soluble sodium salt. Much poorer yields of the hydroxyquinone were obtained by the addition of acetic anhydride to 3,4-phenanthrenequinone and by hydrolyzing and oxidizing the 1,3,4-triacetoxyphenanthrene produced, or by hydrolyzing 3,4-phenanthrenequinone-1-sulfonic acid, though these methods are serviceable in several other instances.

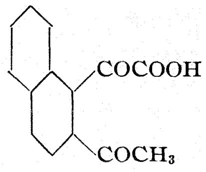
3-Hydroxy-1,4-phenanthrenequinone is very similar in properties to other compounds of the same type, such as hydroxynaphthoquinone or 2-hydroxy-1,4-anthraquinone. Thus the methyl ether may be obtained by the Fischer method of esterification, while interaction of the silver salt of the quinone with allyl bromide yields a mixture of the C-alkylation product, 2-allyl-3-hydroxy-1,4-phenanthrenequinone (63%) and the ortho-quinone ether, 1-alloxy-3,4-phenanthrenequinone (17%).

The Cleavage of 3-Hydroxy-1,4-phenanthrenequinone by Alkali.—While the above-mentioned reactions of the isophenanthrenequinones all belong to well-known types, an entirely novel behavior was discovered when 3-hydroxy-1,4-phenanthrenequinone was subjected to the prolonged action of dilute alkali. The red sodium salt of this quinone is only moderately soluble in water, but when a suspension of the salt in very dilute sodium hydroxide solution was boiled for a few hours in an open beaker the material all dissolved and gave a dull brown-red solution. On acidification a substance separated which dissolved readily in water and crystallized in the form of colorless plates.

The empirical formula of this compound corresponds to that of 3-hydroxy-1,4-phenanthrenequinone plus the elements of water. The substance displaces carbonic acid from its salts, it may be esterified with an alcohol and hydrogen chloride and titration reveals the presence of a single carboxyl group. From these facts it would appear that the quinonoid ring of the hydroxyquinone, IV, has suffered cleavage by the action of a molecule of water. The nature of this cleavage is further elucidated by the fact


IV


V


VI

that the acidic substance yields naphthalene-1,2-dicarboxylic acid on oxidation in alkaline solution by means of hydrogen peroxide. From this it may be concluded that the cleavage of the hydroxyquinone has occurred between the carbon atoms at positions 1 and 2 or at the 2- and 3-positions, or at the 3- and 4-positions. A distinction among these three possibilities is furnished by a consideration of other properties of the cleavage product. This acid melts at 195° and at that temperature loses carbon dioxide; it is not affected by prolonged boiling of its solutions either in dilute acids or alkalies. It is conceivable that the quinone, reacting in a tautomeric, ortho-quinonoid form, might undergo ring rupture at the 1,2-bond, giving V, but this formula is not consistent with the fact that the acid evolves carbon dioxide on melting. The possibility of cleavage between 3 and 4 is ruled out because this would give rise either to a β-keto acid or a β-keto aldehyde (or their enolic forms), and such substances would not possess the observed stability toward mineral acids and alkalies.

On the other hand, the rupture of the ring at the double bond between positions 2 and 3 would yield the α-keto acid, VI, and the properties of the cleavage product are entirely consistent with this formulation. A further confirmation of this structure is furnished by the application of a reaction typical of a-keto acids. It is known that aniline, at an elevated temperature, converts phenylglyoxylic acid into benzalaniline,[3] and α-naphthylglyoxylic acid into the anil of α-naphthaldehyde.[4] In the present instance the cleavage product reacts with one equivalent of aniline at 180° to give a substance having the analysis and properties to be expected for the anil of 2-aceto-1-naphthaldehyde, which indicates that the reaction has followed the normal course

$$C_{10}H_6(COCH_3)(COCOOH) + C_6H_5NH_2 \longrightarrow C_{10}H_6(COCH_3)(CH{=}NC_6H_5) + CO_2 + H_2O$$

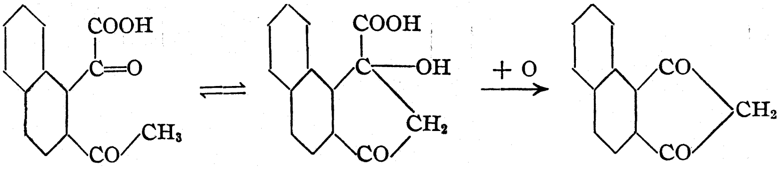
A further reaction of 2-aceto-1-naphthylglyoxylic acid (VI) follows a course which is probably novel. While oxidation in alkaline solution yields naphthalene-1,2-dicarboxylic acid, the action of hydrogen peroxide in glacial acetic acid solution, or of chromic acid in dilute sulfuric acid solution, yields 1,2-naphthindandione, VIII. The identity of this product was established by comparison with an authentic sample prepared by

---

[3] Bouveault, *Bull. soc. chim.*, [3] 15, 1020 (1896); Simon, *Ann. chim.*, [7] **9**, 509 (1896).

[4] Rousset, *Bull. soc. chim.*, [3] 17, **303** (1897).

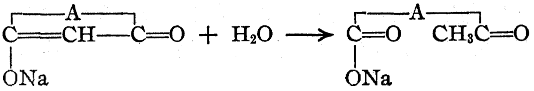
Noto's method.[5] A possible explanation of this rather surprising reaction is given in the following



VI VII VIII

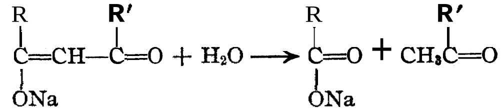
The known ability of the carbonyl group of a-keto acids to enter into aldol condensations lends some plausibility to the hypothesis that the a-keto acid, VI, exists in solution in equilibrium with a small amount of the α-hydroxy acid, VII, while there are many parallels to the conversion of VII into VIII. Thus a-hydroxy-isobutyric acid yields acetone on oxidation,[6] benzilic acid yields benzophenone[7] and a-phenyl-lactic acid, which is the most closely related to the hypothetical acid VII, yields acetophenone.[8]

Only further investigation can determine whether the alkaline cleavage of hydroxyquinones with the production of a carboxyl group and a ketone group in the same molecule is a general reaction, though results to be published shortly demonstrate that at least one other phenanthrene derivative, namely, 2-hydroxy-1,4-phenanthrenequinone, reacts with alkali in the manner indicated with particular ease. It will be noted that these reactions may be represented as follows



$$\overbrace{\underset{\text{ONa}}{\underset{|}{\text{C}}}{=}\text{CH}{-}\text{C}}^{\text{A}}{=}\text{O} + \text{H}_2\text{O} \longrightarrow \overbrace{\underset{\text{ONa}}{\underset{|}{\text{C}}}{=}\text{O}\quad \text{CH}_3\text{C}}^{\text{A}}{=}\text{O}$$

from which the similarity to the alkaline cleavage of a β-diketone, reacting in its enolic form is apparent.



$$\underset{\text{ONa}}{\underset{|}{\overset{\text{R}}{\overset{|}{\text{C}}}}}{=}\text{CH}{-}\overset{\text{R}'}{\overset{|}{\text{C}}}{=}\text{O} + \text{H}_2\text{O} \longrightarrow \underset{\text{ONa}}{\underset{|}{\overset{\text{R}}{\overset{|}{\text{C}}}}}{=}\text{O} + \text{CH}_3\overset{\text{R}'}{\overset{|}{\text{C}}}{=}\text{O}$$

The similarity between the two classes of compounds is not limited to the alkaline hydrolysis; it is quite generally true that hydroxyquinones yield C-alkylation products when the alkylation is carried out with certain particularly reactive alkyl halides9 and 3-hydroxy-1,4-phenanthrenequinone forms no exception to this rule.

In connection with a recent study of the alkaline hydrolysis of β-diketones, Bradley and Robinson[10] have advanced a theory of the mechanism

---

[5] Noto, *Gazz. chim. ital.*, **45,** II, 126, 427 (1915).

[6] Markownikow. Ann., 153,235 (1870).

[7] Jena, *ibid.*, 155, 83 (1870).

[8] Benrath, *ibid.*, 382, 226 (1911).

[9] Fieser, THIS JOURNAL, 48, 3201 (1926); 50, 465 (1928).

[10] Bradley and Robinson, J. Chem. *Soc.*, 2356 (1926).

of the reaction based upon the assumption that the cleavage is a reaction characteristic of the ketonic modification, even though the concentration of this form in an alkaline solution is very small, and without regard to the possible mechanism, or the rate, of the formation of the ketonic modification from the enol. In order to apply these ideas to the cleavage of a hydroxyquinone, one would have to suppose that the salt of this strongly acidic substance undergoes hydrolysis even in the presence of alkali, that the free enol or its ion rearranges into a triketone, and that the latter, purely hypothetical, substance undergoes cleavage. There is little justification for such a view. At the time of the publication of the paper by Bradley and Robinson, their statement that "substances having fixed keto–enolic structures and related to β-diketones are relatively stable to hydroxyl ions," which they cite as evidence in support of their hypothesis of ketonic cleavage, was doubtless justified; but the discovery of the ready cleavage of compounds of fixed enolic structure lends support to the alternate view that it is the enolic modification which suffers cleavage in those cases in which the existence of such a modification is possible.

Experimental Part[11]

4-Amino-3-phenanthrol Hydrochloride.—The amine was prepared by Werner and his students[2] by coupling 3-phenanthrol with diazotized sulfanilic acid and reducing the azo compound with stannous chloride. The process was tedious and in order to convert the aminophenanthrol, which they isolated by extraction with ether, into the hydrochloride, it was necessary to use small quantities of the material. It has now been found that much better results may be obtained by reducing the un-isolated dyestuff with sodium hyposulfite, and that the amine hydrochloride may be prepared on a large scale if proper precautions are taken to prevent oxidation.

Ninety-seven grams of 3-phenanthrol[12] was dissolved in a warm solution of 60 g. of sodium hydroxide in 1.5 liters of water and the solution was cooled by the addition of about 500 g. of ice. A suspension of the diazonium salt was prepared by dissolving 105 g. of crystalline sulfanilic acid in 500 cc. of water and the requisite quantity of alkali, adding 37 g. of sodium nitrite, and pouring the solution into a mixture of 127 cc. of concentrated hydrochloric acid, 200 cc. of water and 500 g. of ice. When diazotization was complete the suspension was poured into the well-stirred phenanthrolate solution. The thick, bright-red solution of the azo compound was allowed to stand for one-half hour, when some solid matter separated, and then a solution of 230 g. of 85% sodium hyposulfite was added and the mixture heated and stirred until the red color disappeared and the aminophenanthrol which separated became very nearly colorless. The product sometimes separated in the form of colorless needles which became slightly yellow on drying and which melted with decomposition at 162° (Werner, 159–161°).

---

[11] The melting points recorded below are all uncorrected. Difficulty was experienced in the analysis of several phenanthrene derivatives, the values for carbon often being as much as 1% too low. This trouble was completely eliminated by the use of a Dennstedt contact star, as recommended by Scholl, *Ber.*, 43, 342 (1910).

[12] New observations concerning the preparation and the alkali fusion of the sulfonates of phenanthrene will be reported in a future communication.

In order to obtain the hydrochloride, the moist amine was made into a fine paste with 2.5 liters of water containing a little sulfur dioxide, 95 cc. of concentrated hydrochloric acid was added and the mixture was heated and stirred until all but a very small quantity of black, tarry material dissolved. On adding hydrochloric acid to the filtered solution, while still hot, 4-amino-3-phenanthrol hydrochloride separated in the form of pale gray needles; yield, 113 g. (92%).

The material prepared in the manner indicated may be preserved indefinitely without undergoing any change, but a less pure product rapidly becomes green. The free amine is very sensitive to the oxidizing action of the air and to heat and it is largely destroyed if an attempt is made to dissolve the dry material in water containing just one equivalent of hydrogen chloride. A considerable excess of acid is required to prevent hydrolysis. These facts may serve to explain Werner's difficulty in preparing the pure salt in quantity.

3,4-Phenanthrenequinone.—Oxidation of 4-amino-3-phenanthrol hydrochloride with chromic acid in aqueous solution or suspension gave a product which was contaminated by considerable black, insoluble material. Though this may be removed by extracting the quinone with alcohol and precipitating it with water, the following method of oxidation gives a product which is practically pure at the outset, provided that the amine salt is pure and that the conditions are carefully controlled as specified.

Twelve grams of 4-amino-3-phenanthrolhydrochloride was made into a fine paste with 120 cc. of glacial acetic acid at room temperature. A thermometer was placed in the mixture, an ice-bath was made ready and a solution of 5 g. of chromic anhydride in water was added all at once. The mixture was stirred vigorously and the temperature was not allowed to rise above 40°. The salt rapidly dissolved and formed a deep red solution. After ten minutes the solution was poured into 500 cc. of water, thus precipitating the quinone in the form of *a* very fine, orange-red suspension which soon coagulated to a spongy precipitate which was easily collected and washed free of acid. The yield was 8.9 g. (87%) and the quinone was very nearly pure.

Slight variations from these conditions, such as a change in the initial or the maximum temperature or the gradual addition of the oxidizing agent, gave, in poorer yield, a darker product which was collected and washed with great difficulty, for a very fine, black substance partially clogged the filter paper and rendered the filtrate black. The quinone is also produced by the action of nitrous acid on a suspension of the amine hydrochloride but it rapidly undergoes decomposition to a black tar.

3,4-Phenanthrenequinone is best crystallized from a mixture of benzene and ligroin. On rapid cooling the solution deposits a spongy product; excellent, long, brilliant red needles are produced on cooling slowly. In agreement with the observation of Barger,[1] the substance was found to melt with decomposition at 133°.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Found: C, 80.35; H, 4.06.

The reaction of this quinone with sulfuric acid constitutes a highly characteristic test, for a solution of the substance in the concentrated acid at first has a beautiful Prussian blue color which changes in a few minutes to a clear, chrome green. The rate of the change is dependent upon the purity of the sample and also upon the amount of acid employed. Mixed with a very small quantity of acid, the pure quinone gives a blue color which lasts less than one minute; using a large volume of acid, it persists for several minutes. When the uncrystallized quinone is added to a large volume of acid, the blue stage has only a momentary existence.

Morphol is conveniently prepared by reducing the quinone with an aqueous solution of sodium hyposulfite or sulfur dioxide, while diacetylmorphol is best obtained by boiling a mixture of 10 g. of the quinone, 10 g. of zinc dust, 10 g. of fused sodium acetate and 80 cc. of acetic anhydride until no further color change occurs. The mixture is then diluted with glacial acetic acid, filtered and cautiously treated with water. Crystallization from benzene gives a pure product (10.8 g.) melting at 158° (Barger, 158°). Vongerichten has described the conversion of this substance into diacetylmorpholquinone.[13] The author's experiments confirmed his statement regarding the yield and the pure material was found to melt at 197° (Vongerichten, 196°).

The Addition of Sodium Bisulfite to 3,4-Phenanthrenequinone.—This reaction, which proceeds so readily in the case of β-naphthoquinone, at first presented some difficulties. Since the phenanthrenequinone is very easily destroyed by acids, much of the material is converted into an insoluble, black substance unless the bisulfite solution is concentrated enough so that the addition reaction becomes very rapid. Thus, while the quinone dissolves only partially in dilute bisulfite solution, it is almost completely soluble in a saturated solution and, after time has been allowed for the rearrangement of the primary addition product, the sulfonic acid formed may be isolated in the form of an amine salt or else oxidized to a sulfonated quinone.

Ammonium 3,4-Phenanthrenequinone-1-sulfonate.—Twenty and eight-tenths grams of uncrystallized 3,4-phenanthrenequinone was ground to a fine paste with 150 cc. of water and 41.6 g. of sodium bisulfite was added all at once while the mixture was stirred thoroughly. Nearly all of the quinone dissolved, giving a thick, dark-brown solution. After standing for a few hours, it was diluted with water to a volume of 250 cc., 8.5 cc. of concentrated sulfuric acid was added cautiously, together with a few drops of caprylic alcohol to disperse the foam, and the solution was heated until the sulfur dioxide had been driven off. The solution was then filtered through a folded paper in order to remove a little dark material, cooled to room temperature and treated with a chromic acid solution containing 15 g. of the anhydride and 15 cc. of concentrated sulfuric acid. To the deep-red solution of the quinone a saturated solution of sodium chloride was added, causing the separation of a partially gelatinous precipitate of sodium 3,4-phenanthrenequinone-sulfonate. In spite of the dispersed character of the precipitate, no difficulty was experienced in collecting it and in pressing it free of most of the water, though it was not obtained in a condition satisfactory for analysis. The ammonium salt, although it is rather unstable, forms good crystals. It was prepared by adding saturated ammonium chloride solution to a hot solution of the sodium salt and cooling the solution rapidly. Small, glistening, dark red plates were thus obtained; yield: 18.5 g. (about 53% of the theoretical amount).

The salt is not easily crystallized. A hot solution in pure water turns dark before crystals begin to separate and even when an ammonium salt is added to decrease the solubility, a dark red, insoluble substance is formed unless the solution is cooled rapidly and unless the crystals are separated from the solvent without delay. The air-dried material contained about 13% of water and the anhydrous salt is very hygroscopic.

---

[13] Vongerichten, *Ber.*, 32, 1521 (1899).

Anal. Calcd. for $C_{14}H_{11}O_5NS$: S, 10.50. Pound: S, 10.58.

p-Toluidine Salt of 3,4-Dihydroxyphenanthrene-1-sulfonic Acid.—The sodium and potassium salts of the acid are extremely soluble in water, but the p-toluidine salt crystallized readily on adding a solution of the amine hydrochloride to the solution of the dihydroxyphenanthrene-sulfonate obtained by the addition of sodium bisulfite to 3,4-phenanthrenequinone or by the reduction of the sulfonated quinone. The compound dissolves readily in water and crystallizes in the form of colorless needles which become slightly gray on drying and which decompose at about 182".

And. Calcd. for $C_{21}H_{19}O_5NS$: C, 63.45; H, 4.82. Found: C, 63.44; H, 5.03.

1-(p-Toluidino)-3,4-phenanthrenequinone.—This compound soon precipitated when aqueous or alcoholic solutions of equivalent quantities of ammonium 3,4-phenanthrenequinone-1-sulfonate and p-toluidine were combined and heated for a short time. A brick-red product was thus obtained in 60% yield. It is sparingly soluble in alcohol; somewhat more so in glacial acetic acid or toluene. It dissolves in alcoholic sodium hydroxide solution with a red color but it is insoluble in aqueous alkali. Crystallized from xylene the substance formed a crust of small, dark red crystals which melted with decomposition at 260°.

Anal. Calcd. for $C_{21}H_{15}O_2N$: C, 80.48; H, 4.83. Found: C, 80.29; H, 5.01.

1-(p-Toluidino)-3,4-diacetoxyphenanthrene was prepared by the reductive acetylation of the above quinone with zinc dust, sodium acetate and acetic anhydride. It is only sparingly soluble in alcohol, but readily soluble in benzene or glacial acetic acid. The benzene solution is fluorescent and it deposits short, colorless needles melting at 208°.

Anal. Calcd. for $C_{25}H_{21}O_4N$: C, 75.16; H, 5.30. Found: C, 75.09; H, 5.60.

3-Hydroxy-1,4-phenanthrenequinone.—Several methods of hydroxylating 3,4-phenanthrenequinone were investigated and the less successful procedures may be mentioned briefly. The Thiele reaction, which involves the addition of acetic anhydride to the quinone molecule under the influence of sulfuric acid, gave very poor resuits, probabiy because the quinone is extremely sensitive to the action of mineral acids. Even at room temperature the reaction yielded only a black, tarry product which gave a certain amount (30%) of the hydroxyquinone on hydrolysis, air oxidation and purification through the sodium salt, but from which pure 1,3,4-triacetoxy-phenanthrene could not be isolated.

A second method, which has given good results with similar compounds,[9b,14] consisted in the conversion of ammonium 3,4-phenanthrenequinone-1-sulfonate into 3-methoxy-1,4-phenanthrenequinone (see below), and hydrolyzing this ether. Thus a suspension of 5 g. of the ammonium salt in 25 *cc.* of methyl alcohol was treated with 4 cc. of concentrated sulfuric acid, while shaking, and the mixture was then allowed to cool. The ether which separated, washed with water and with a little alcohol, was nearly pure, and it gave a 97% yield of the pure hydroxyquinone on hydrolysis. The yield was only 2 g., or 59% of the theoretical amount, so that the overall yield of the hydroxy compound from 3,4-phenanthrenequinone was only 30%.

---

[14] Fieser, THIS JOURNAL, 48,2929 (1926).

A much simpler process, which gave a better yield of material, consisted in oxidizing 3,4-dihydroxyphenanthrene-1-sulfonic acid in alkaline solution with air or, better, with hydrogen peroxide. It is convenient to start with 4-amino-3-phenanthrol hydrochloride and not to isolate any of the intermediates in dry form.

Twelve grams of this amine salt was oxidized in the manner indicated above and the 3,4-phenanthrenequinone (average dry weight, 8.9 g.) was made into a paste with 100 cc. of water; 16 g. of sodium bisulfite was added and, after one-half hour, 4 cc. of concentrated sulfuric acid was added cautiously; the sulfur dioxide was boiled off and the filtered solution of sodium 3,4-dihydroxyphenanthrene-1-sulfonate was treated with 70 cc. of 6 *N* sodium hydroxide solution and 100 cc. of 3% hydrogen peroxide solution. A red precipitate of the sodium salt of 3-hydroxy-1,4-phenanthrenequinone soon began to separate and it was collected after a few hours. The addition of more peroxide to the filtrate usually gave a further quantity of the salt. The combined product was dissolved in boiling water, the red solution was quickly filtered from a small amount of black material and acidified, when the hydroxy compound separated in the form of a very fine yellow suspension. This material is very pure. The yield was 5.6 g., or 58% of the theoretical amount based on the weight of aminophenanthrol hydrochloride.

3-Hydroxy-1,4-phenanthrenequinone is only very sparingly soluble in water; it dissolves readily in alcohol or benzene and very readily in glacial acetic acid. The solution in concentrated sulfuric acid is brown-red, while the alkaline solution is red. The sodium salt is very sparingly soluble in the presence of an excess of alkali. The hydroxy compound is a strong acid, being soluble in sodium acetate solution. It was crystallized repeatedly from benzene and from dilute acetic acid, when it formed small, orange-yellow needles which sintered at 200° and melted, with some decomposition, at 230".

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.87; H, 3.67.

3-Methoxy-1,4-phenanthrenequinone.—The preparation of this ether from ammonium 3,4-phenanthrenequinone-1-sulfonate has been described above. It was also obtained by boiling a solution of the hydroxy compound in methyl alcohol containing a little hydrogen chloride. The ether soon separated in crystalline condition. It was crystallized from alcohol and from benzene-ligroin, forming light yellow needles melting at 170".

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.69; H, 4.40.

3-Methoxy-1,4-diacetoxyphenanthrene was obtained in 91% yield by the reductive acetylation of the above ether. Crystallized repeatedly from benzene–ligroin, it formed clusters of stout, colorless needles, m. p. 168.5".

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.35; H, 4.98. Found: C, 70.14; H, 5.15.

An attempt to obtain a pure oxidation product of this substance was unsuccessful, though there were indications of the formation of a small amount of a phenanthrenequinone.

The Allylation of 3-Hydroxy-1,4-phenanthrenequinone.—The hydroxy compound was converted into its dark red silver salt by adding silver nitrate to a neutral solution of the ammonium salt at 60°.

Anal. Calcd. for $C_{14}H_7O_3Ag$: Ag, 32.59. Found: Ag, 32.60.

A suspension of 6.7 g. of this salt in 100 cc. of benzene was treated with 2.7 g. of allyl bromide and heated to boiling for forty-five minutes, when the reaction was complete. Only two products were isolated: 1-alloxy-3,4-phenanthrenequinone and 2-allyl-3-hydroxy-1,4-phenanthrenequinone. The former crystallized on concentrating the benzene solution, whiie the latter was extracted from the benzene solution with ammonia solution; yields: 63 and 17%, respectively. A *p*-quinone ether appeared to be present in small quantity, but it was not obtained in pure form.

1-Alloxy-3,4-phenanthrenequinone is readily soluble in alcohol or benzene and crystallizes in the form of brilliant orange needles melting at 161°. While it is not soluble in bisulfite solution, it is completely hydrolyzed by dissolution in alcohol containing a little hydrochloric acid, a reaction characteristic of o-quinone ethers of this type.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.10; H, 4.56.

2-Allyl-3-hydroxy-1,4-phenanthrenequinone dissolves readily in glacial acetic acid or alcohol but it does not crystallize well from these solvents. The solution in ligroin deposits light sponges of small, orange needles, m. p. 155°.

And. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.22, H, 4.60.

This C-alkylation product may also be prepared in good yield by heating 1-alloxy-3,4-phenanthrenequinone to a temperature just above the melting point. Like other substances of this type the compound dissolves in alkali with a red color and it is converted into the following heterocyclic derivative by sulfuric acid.

1-Methyl-5,6-(1,2-naphtho)-3,4-quinone resulted when 1 g. of the above quinone was dissolved in 5 cc. of cold, concentrated sulfuric acid and the solution poured into a large volume of water. The flocculent, red precipitate was crystallized several times from benzene–ligroin with the use of animal charcoal and it was thus freed of a little tar and obtained in the form of brilliant red, flat needles melting at 198–199°. It is insoluble in bisulfite solution.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 76.98; H, 4.56.

The **Action of Alkali on 3-Hydroxy-1,4-phenanthrenequinone.**—The hydrolytic cleavage of this quinone may be accomplished by prolonged boiling of a solution of the sodium sait in water, but the reaction is hastened by the presence of an excess of alkali. Thus a suspension of 8 g. of the pure sodium salt in 3 liters of water containing 20 cc. of 6 N sodium hydroxide solution was boiled gently in an open beaker until all of the solid had dissolved, the clear red color had given place to a dull red-brown and the volume had been dimished to about 400 cc. This required about four hours. A small amount of dark material was then separated by filtration and the solution was acidified with hydrochloric acid while still hot. A part of the material separated in the form of an oil which soon solidified, while part formed large plates. Concentration of the mother liquor yielded an additional quantity of this substance. The combined product, on crystallization from dilute hydrochloric acid with the use of animal charcoal, yielded 5.7 g. (82%) of slightly brown, but essentially pure, material.

This substance, which has been identified as 2-aceto-1-naphthylglyoxylic acid (VI), was freed of all traces of coloring matter only after repeated crystallization from acidified water, though this process did not alter the melting point. The pure material melts at 196° with the rapid evolution of carbon dioxide and passes into a glassy substance. It dissolves readily in hot water and crystallizes, best in the presence of a mineral acid, in the form of large, colorless plates. The solubility in cold water is quite appreciable. On acidification of a dilute aqueous solution of the sodium salt the compound separates very slowly but in the form of excellent crystals. The acid decomposes sodium carbonate; it is very sparingly soluble in benzene, moderately soluble in ether and very readily soluble in alcohol.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.41; H, 4.16. Found: C, 69.41; H, 4.26. *Neut. Equiv.* Subs., 0.1716: 5.74 cc. of 0.1242 N $Ba(OH)_2$. Calcd. for $C_{14}H_{10}O_4$: mol. wt., 242.1. Found: 240.7.

The methyl ester was easily obtained by boiling a solution of the acid in methyl alcohol containing hydrogen chloride. After removal of most of the alcohol the addition of water caused the separation of an oil which soon solidified. The ester dissolves readily in benzene and only sparingly in ligroin; it crystallizes well from a mixture of the two solvents, forming small, colorless prisms melting at 181". It does not react with sodium bisulfite to any appreciable extent and it is indifferent toward bromine or ferric chloride.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.56; H, 4.88.

Oxidation of the Cleavage Product in Alkaline Solution.—A solution of 0.5 g. of 2-aceto-1-naphthylglyoxylic acid in 4 cc. of 5% sodium hydroxide was treated with 2 cc. of perhydrol and the solution was kept at a temperature of 60° for several hours. The oxidation was not complete, for some of the unchanged acid separated in the form of a dark tar on acidification. After this had been removed and the solution boiled with animal charcoal and well concentrated, small, colorless crystals of naphthalene-1,2-dicarboxylic acid melting at 175° were obtained. The material was purified by crystallization of the sparingly soluble acid potassium salt and then crystallized from water. The acid melted at 175° with loss of water; the anhydride so produced melted at 165". These properties agree with Cleve's description[15] of naphthalene-1,2-dicarboxylic acid.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.66; H, 3.73. Found: C, 66.46; H, 3.76.

Oxidation of the Cleavage Product in Acid Solution.—To a boiling solution of 1 g. of 2-aceto-1-naphthylglyoxylic acid in a mixture of 75 cc. of water and 4 cc. of concentrated sulfuric acid, a solution of 0.4 g. of potassium dichromate was gradually added. Oxidation took place rapidly with the evolution of carbon dioxide and the separation of a yellow substance which was found to be 1,2-naphthindandione (VIII). After one crystallization from alcohol, long, slender, yellow needles melting at 174–175° were obtained; yield, 0.6 g. The same substance was obtained, though in poorer yield, by boiling a solution of 2 g. of the glyoxylic acid in 12 cc. of glacial acetic acid with 5 cc. of perhydrol for one hour.

Samples of 1,2-naphthindandione were crystallized from a variety of solvents such as alcohol, glacial acetic acid and benzene-ligroin; the melting point always remained constant at 174–175° and the crystals were distinctly yellow. On solution of the crystallized material in alkali, however, a small amount of colored impurity remained undissolved and the material precipitated by acidification and crystallized from benzene–ligroin was now only very faintly yellow but still melted at the same temperature.

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.57; H, 4.02. Found: C, 79.45; H, 4.18.

The alkaline solution of the compound is deep red; the solution in concentrated sulfuric acid is yellow. It reacts with benzaldehyde in the presence of a trace of pyridine to give a product which forms small, lemon-yellow needles melting at 179°. The properties of the diketone correspond very closely with the description of 1,2-naphthin-

---

[15] Cleve, Ber., 25, 2475 (1892).

dandione given by Noto,[5] who synthesized this compound from naphthalene-1,2-dicarboxylic acid, except that the melting point of 174–175° is lower than the figure of 180° recorded by the Italian investigator, and that the benzal derivative was found to melt at 179°, instead of at 190°. The identity of the two compounds was definitely established, however, by comparing the material obtained in the present research with a sample prepared by Noto's method. Each sample, as well as a mixture of the two, melted at 174–175°.

The Action of Aniline on 2-Aceto-1-naphthylglyoxylic Acid.—Two and one-half grams of the acid was dissolved in ether, 0.98 g. of aniline added and the solution evaporated to dryness. The solid residue was transferred to a small flask and this was evacuated with the use of an oil pump and heated in an oil-bath. At 175° the material commenced to fuse with the evolution of gas and a thick, dark-brown liquid soon resulted. After heating at 175–180° for ten minutes, the flask was cooled and the product crystallized from benzene. The dark-brown impurities are largely retained in the mother liquor, for clean, yellow crystals of the nearly pure reaction product separated from the solution on cooling and a further quantity was obtained on concentrating the mother liquor; yield, 1 g.

2-Aceto-1-naphthalaniline is readily soluble in benzene, moderately soluble in alcohol or ether and sparingly soluble in ligroin or water. A sample for analysis, crystallized from benzene and from ethyl acetate, formed small, yellow needles melting at 202°.

Anal. Calcd. for $C_{19}H_{15}ON$: C, 83.48; H, 5.53. Found: C, 83.14; H, 5.72.

The compound is insoluble in alkali; it dissolves in concentrated sulfuric acid to give a solution exhibiting an intense green-yellow fluorescence. On addition of a small amount of water, the fluorescence disappears and a colorless salt soon crystallizes from the clear solution. The salt decomposes on further dilution with the formation of the yellow anil.

The author takes pleasure in acknowledging a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for the purchase of the phenanthrene used in this investigation and in other studies to be reported shortly.

Summary

1. 3,4-Phenanthrenequinone may be obtained in quantity and in good yield by converting 3-phenanthrol into an azo dye, reducing the azo compound and oxidizing the 4-amino-3-phenanthrol so produced. The quinone adds a molecule of sodium bisulfite and the resulting product may be converted into 3-hydroxy-1,4-phenanthrenequinone. The alkylation of this hydroxyquinone follows the normal course.

2. When 3-hydroxy-1,4-phenanthrenequinone is boiled with dilute alkali, the quinonoid ring suffers hydrolytic cleavage in a manner entirely analogous to the cleavage of β-diketones.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

PHOSPHORIC ACID ESTER DERIVATIVES OF CHOLINE. BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF -ONIUM COMPOUNDS. VIII[1]

BY R. R. RENSHAW AND C. Y. HOPKINS

RECEIVED JANUARY 24, 1929 PUBLISHED MARCH 6, 1929

The phosphoric acid ester of choline and its derivatives are of interest not only because of their relationship to lecithin and because of a possible utilization of them in the synthesis of the latter substance, but also on account of the pharmacological properties that some of them may have.

Our earlier work on attempts to prepare phosphoric acid ester derivatives of choline[2] convinced us that these could not be obtained readily by double decomposition reactions with iodo- or bromo-ethyltrimethylammonium salts, nor by the action of phosphoric halides on choline. Much better prospects for obtaining these products as well as for the synthesis of the structure usually assigned to lecithin seemed possible by starting with β-chloro-ethyl phosphoryl dichloride $ClCH_2CH_2OPOCl_2$. This product was obtained in coöperation with Mr. Shott in this Laboratory in 1926, and during the winter of 1927–1928 the products herein described were prepared. We expected to extend this work before publishing, but since others have entered the field[3] it seems desirable to present the material at this time.

β-Chloro-ethyl Phosphoryl Dichloride, $ClCH_2CH_2OPOCl_2$.—A mixture of 80.5 g. (1 mole) of ethylene chlorohydrin and 100 cc. of dry carbon tetrachloride was stirred vigorously while 153.5 g. (1 mole) of phosphoryl chloride was added through a dropping funnel over a period of one and one-half hours. The stirring was continued while the flask was heated on the water-bath for three hours. The mixture was then distilled very carefully under diminished pressure, with the temperature being kept below 60° until the carbon tetrachloride was removed and hydrogen chloride no longer was evolved. The product distilled at 108–110° (15 mm.) in a yield of 91 to 93 g. (46 to 47% of the theoretical). It is a colorless, mobile liquid of suffocating odor.

Anal. Calcd. for $C_2H_4O_2Cl_3P$: Cl, 53.86. Found: CI, 54.14, 53.89.

This dichloride condensed readily with trimethylamine under anhydrous conditions to form a very hygroscopic product which was probably dichlorophosphato-ethyltrimethylammonium chloride, isomeric with the product isolated by the action of phosphoryl chloride on choline.

Dimethyl (3-Chloro-ethylPhosphate, $ClCH_2CH_2OPO(OCH_3)_2$.—To a rapidly stirred mixture of 29.5 g. (0.15 mole) of β-chloro-ethyl phosphoryl dichloride and 50 cc. of dry

---

[1] This problem is being carried on in cooperation 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] Renshaw and Ware, THIS JOURNAL, 47, 2993 (1925).

[3] Our attention has just been called to a report of a paper on "Esters of Phosphoric Acid," presented before the Biochemical Society by Plimmer and Burch, in which they describe (3-chloro-ethyl phosphoryl dichloride.

carbon tetrachloride contained in a flask surrounded by cold water, there was added drop by drop 12 g. (0.37 mole) of absolute methyl alcohol. The reaction mixture was refluxed gently for one to two hours until no more hydrogen chloride was evolved. The solvent was then removed by evaporation under a vacuum and the remaining liquid fractionated at a pressure of 4 mm. Considerable decomposition resulted at higher pressures. There was finally obtained 7 g. (25% yield) of the desired ester boiling at 95–96° (4 mm.). Dimethyl β-chloro-ethyl phosphate is a colorless, mobile liquid having a faint ester odor.

Anal. Calcd. for $C_4H_{10}O_4PCl$: Cl, 18.79. Found: Cl, 18.94, 18.70.

Dimethylphosphato-ethyltrimethylammonium Chloride (Choline Ester of Dimethyl Phosphoric Acid), $(CH_3O)_2OPOCH_2CH_2N(CH_3)_3Cl$.—A toluene solution of 3.0 g. (0.05 mole) of trimethylamine and 9.4 g. (0.05 mole) of dimethyl β-chloro-ethyl phosphate was allowed to stand overnight in a pressure bottle. The product was filtered off and washed with toluene and dry ether. It crystallized from a small volume of chloroform in fine needles, m. p. 136.5–137° (corr.). It is somewhat soluble in chloroform and acetic anhydride, very soluble in water and in ethyl alcohol, nearly insoluble in ether, toluene, petroleum ether and carbon tetrachloride. It is very hygroscopic.

Anal. Calcd. for $C_7H_{19}O_4NClP$: Cl, 14.32. Found: Cl, 14.42, 14.37.

Dr. Reid Hunt has found this compound to have little muscarine action. It does have, however, a powerful stimulating nicotine action.

Conclusion

β-Chloro-ethyl phosphoryl dichloride has been prepared. It condenses with trimethylamine to form a quarternary salt. From it, too, dimethyl β-chloro-ethyl phosphate has been obtained. This forms with trimethylamine the choline ester of dimethylphosphoric acid. Hunt has found that the latter compound has the interesting property of giving a powerful stimulating nicotine action and yet has little muscarine action.

NEW YORK, N. Y.

NEW BOOKS

College Chemistry. BY NEIL E. GORDON, Professor of Chemical Education, Johns Hopkins University. World Book Company, Yonkers-on-Hudson, New York, 1928. ix + 516 pp. 88 figs. 14 X 21 cm. Price $2.96.

The book is written especially for students who have had high-school chemistry and therefore omits much of the descriptive material found in ordinary texts. It is divided into two general parts, the non-metals and the metals. Under each head certain units are taken up, since it is the idea of the author that for students who already have a reasonable amount of chemical information, the more advanced viewpoint is best given by the study of topics rather than by a description of the properties of individual elements. Like other Gordon texts, the subject is presented by means of laboratory exercises, on which the discussion is based. While this may make the book less generally useful than if it were cast in the usual form, yet it has advantages for those who wish to follow Dr. Gordon's methods exactly. In general, standard methods of presentation have been used. The author should be commended for his practice of presenting problems without excessive use of formulas. It is doubtful, however, whether the terms electronization and deëlectronization will ever take the place of the historical reduction and oxidation. The book is carefully written and well arranged and undoubtedly is a real addition to the texts available for the teaching of chemistry.

P. A. BOND

Anleitung zur Chemischen Gesteinsanalyse. (Introduction to Chemical Rock Analysis.) By PROF. DR. J. JAKOB. Gebriider Borntraeger, W 35 Schöneberger Ufer 12 a, Berlin, Germany, 1928. vii + 81 pp. 3 figs. 16 × 24.5 cm. Price, bound, R. M. 7.

This "Biichlein" attempts to instruct the student in the making of the complicated chemical analysis of rocks, by which igneous rocks are mostly meant, within the compass of 79 pages. There is no general discussion of apparatus, reagents, methods or sources of error, and much of the matter is relegated to the footnotes. The student is assumed to have some knowledge of general quantitative analytical procedure or to work under the supervision of an instructor.

The methods, in general, follow those of Hillebrand and of the reviewer, but there are many complications and variations, and several of these differences in procedure are wide and unexpected, some of them not for the better. The treatment is very unbalanced: some of the descriptions are ultra-detailed, while again an important determination is dealt with much too briefly. Thus, only one page is devoted to the method for FeO, while two pages are given to the unimportant Li_2O. The reviewer differs with the author as to many particulars, such as the use of a porcelain basin ("which should not be much attacked") for treating the sodium carbonate melt; the advocacy of the old and very inaccurate and tedious Cooke method for FeO instead of the rapid and accurate Pratt method; the use of H_2SO_4 instead of HCl in several processes; the inordinate quantities of hydrofluoric acid that are recommended; the non-use of molten pyrosulfate for bringing the ignited Al_2O_3, etc., precipitate into solution; and the details of many other procedures too numerous to be mentioned here. The author advocates the determination of several constituents in aliquot parts of a filtrate. This is usually quite unnecessary, for the amount of rock powder available is, or should be, sufficient to make many of the author's material-saving procedures uncalled for, although they may often be necessary in analyzing a mineral of which there may be only a gram or so. The author lays much stress on accuracy, but the attainment of this is, in many cases, rendered difficult by the elaborate and complicated precautions that are taken especially to ensure it. The book, on the whole, is distinctly disappointing and, as a modern textbook, does not compare favorably with the earlier ones by Dittrich and by Jannasch.

The reviewer takes this opportunity to deplore the very inadequate and unsatisfactory way in which the quantitative analysis of silicates, including rocks and minerals, is treated in the standard manuals of quantitative analysis, such as those of Fresenius and of Treadwell-Hall.

HENRY S. WASHINGTON

Physikalisch-chemische Praktikumsaufgaben. (Experiments in Physical Chemistry.) By DR. ARNOLD EUCKEN, Professor and Director of the Physical-Chemical Institute of the Technical High School of Breslau, and Dr. Rudolf Suhrmann, Lecturer at the Technical High School of Breslau. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 4, Leipzig C 1, Germany, 1928. xii + 240 pp. 103 figs. 16 × 23 cm. Price, unbound, M. 13; bound, M. 14.

This Laboratory manual is undoubtedly the best that has so far been published. The experiments are, in the main, well chosen to illustrate the principles of physical chemistry, and are sufficient in number to allow the instructor considerable latitude in the way of choice of the experiments to be assigned. The directions, while brief, are sufficiently explicit, and an abundance of references are given so that the student who has a real curiosity (and some do exist) can easily learn more concerning the subject. The typography and binding are both excellent.

Part I is an introduction to the various methods of physico-chemical measurement and includes 24 experiments. Part II is devoted to physico-chemical analyses by mechanical, optical, thermal and electrical methods. Fourteen well-chosen experiments illustrate the use of such methods for quantitative analytical work. Doubtless some will consider that much of this should be given in a course entitled, say, "Quantitative Analysis by Instrumental Methods." The important point is that it be given somewhere. Part III is devoted to the determination of physical chemical constants and includes 59 experiments grouped under the general headings: thermal constants (26 experiments), calorimetric measurements (6 experiments), reaction velocity (4 experiments), electrolytic constants (8 experiments), surface phenomena (7 experiments), and the constitution of matter (8 experiments). Among these many experiments are a considerable number which are essentially new, and while the reviewer has not had an opportunity to try them out in the laboratory, he sees no reason why they should not work out satisfactorily. Part IV is an Appendix in which ten additional experiments are suggested. The student is expected to work out his own details of procedure from the literature references and hints given.

A laboratory course based on the performance of all of the experiments given would probably run through a period of two years, which is more time than can usually be devoted to this subject. However, with such an excellent assortment from which to choose, the instructor should be able to plan assignments of 30 to 40 experiments for a year's course for each student, and at the same time to vary the assignments so as to have most of the experiments going on in the laboratory. Students learn much by association, and the reviewer believes that nothing is more deadly than to have each student in a class perform exactly the same list of experiments. Such a system savors too much of machine production. The greater the variety of the experiments going on in the laboratory, the more interest on the part of the students (and instructor).

J. H. MATHEWS

Das Gesetz der chemischen Massenwirkung. Seine Thermodynamische Begründung und Erweiterung. (The Law of Chemical Mass Action. Its Thermodynamic Basis and Development.) By RICHARD LORENZ, Dr. Phil., Dr. Ing. E.H., Professor and Director of the Physical Chemistry Institute of the University of Frankfort. Leopold Voss, Solomonstrasse 18 B, Leipzig, Germany, 1927. x + 176 pp. 13 figs. 16 × 23.5 cm. Price, unbound, R. M. 12.50; bound, R. M. 14.50.

This monograph presents the results of the experimental work of the author and his collaborators on the equilibrium between molten metals and their salts (chlorides), all being of the type $Pb + CdCl_2 = Cd + PbCl_2$, in which there are two immiscible liquid phases. A thermodynamic development of a mass action law for such condensed systems is given, using van Laar's and the author's equations for the chemical potential of gases in gas mixtures.

The classical mass action law of Guldberg and Waage is discussed at length, giving the van't Hoff derivation and several applications. The chemical potential of a gas in a mixture of ideal gases is next developed and the "ideal mass action" law again derived by use of the general equilibrium relation $\Sigma\ (\nu_1\, \mu_1) = 0$. An equation for the chemical potential of a gas in a mixture of gases obeying van der Waals' equation is then obtained by use of the thermodynamic potential $F_{V,T}$, and applied to condensed (liquid) systems by replacing the volume of the gas by the van der Waals' B constant for the mixture. The "new mass law" deduced in this manner is applied to some nine equilibria between molten metals and their chlorides with fair success. Finally a discussion of the Duhem–Margules relation and the electromotive force of cells composed of molten salts and metals is given.

The logic of the treatment of mixtures of gases obeying van der Waals' equation is not satisfying, although the expression given for the chemical potential can be deduced by use of the more rigorous methods developed by Gillespie and others. The author's derivation is not made with a minimum of assumptions and in fact those assumptions which are used are not clearly stated. Since the treatment of condensed systems requires an integration along the van der Waals' isotherm into the liquid phase, the new mass action law so obtained can hardly be considered as resting on a firm thermodynamic basis and must stand or fall on its simplicity and reproduction of the experimental data.

The monograph contains a wealth of historical information, especially that derived from German sources. Much material which does not bear on the author's main thesis and which is to be found in textbooks on physical chemistry is included.

JAMES A. BEATTIE

Atomic Structure as Modified by Oxidation and Reduction. By WILLIAM COLEBROOK REYNOLDS, D.Sc. (Lond.), **F.I.C.,** A.R.C.S. **Longmans, Green and Company, 55 Fifth Avenue, New York, 1928. viii + 128 pp. 11 figs. 14 × 22.5 cm. Price, $3.00.**

This book presents a scheme of electron distribution in atoms which is at variance with those now considered generally useful or probable. The author shows a hearty indifference to spectroscopic or other verifications of his proposed structures, but applies these to the "explanation" of a wide variety of facts of inorganic and organic chemistry. As the rules of the game are not very clearly stated, it is hard to appraise the theory's triumphs in these fields. The sections on the" emission and absorption of radiation, the structure of solid conductors and magnets, are entirely qualitative and vague, and appear to offer no advantages over treatments based on quantum theory. No book of this type can be complete without a little something about the ether, and accordingly we learn that "the chemistry of the ether has been neglected" and come to know "the properties of ether particles," and that "on account of these," e. g., it is not m but e which varies at high electronic speeds. Stress and strain, dielectric constants, photoelectricity, gravitation, special and general relativity and many other topics are one by one seized, licked into shape in a few terse sentences and returned to their guardians, the physicists, with a grave word or two of warning or encouragement. It seems a pity that a book of such wide scope should bear *a* title which might mislead a prospective purchaser into expecting another mere Sommerfeld or Andrade. The reviewer begs to take as his motto a clause from page 123 "At present we must try and appraise aberrations correctly."

NORRIS F. HALL

Lumineszenz-Analyse im filtrierten ultravioletten Licht. (Analysis by Means of Luminescence in Filtered Ultraviolet Light.) By PROFESSOR DR. **P.** W. DANCKWORTT, **Hannover. Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1928.** vii **+ 106 pp. 39 figs. 16 × 23.5 cm. Price, unbound, M. 6.50; bound, M. 7.80.**

Inorganic and organic substances in truly great variety fluoresce in that part of the invisible radiation of the quartz mercury vapor lamp which is transmitted by nickel oxide glass, Differences in color and intensity including, of course, absence of fluorescence, lead to qualitative identifications and even to quantitative data. It is evident that comparisons involving several monochromatic and widely separated spectral bands would be even more highly informative. The book outlines microscopic as well as macroscopic procedures, and does not neglect photographic possibilities. Gems, minerals, fossils, textiles, rubber, dyestuffs, foods, drugs, anatomical preparations and bacteria are examples of the materials discussed. The section on criminal investigation ought to provide plots for a wealth of detective stories involving secret writings, counterfeited or altered money, stamps, checks and other documents, finger prints, physiological secretions and the like. Some two hundred selected references are given in conclusion. The author, enthusiast though he is, stresses the uncertainties of his art, especially in inexperienced hands. The general interest of the book will amply repay the reader, even if it touches upon none of his scientific or personal problems.

G. S. FORBES

Chemical Publications, their Nature and Use. By MELVIN GUY MELLON, Ph.D., **Associate Professor of Analytical Chemistry, Purdue University. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1928. viii + 253 pp. 14.5 × 21 cm. Price, $2.50.**

About a year or so ago, Crane and Patterson published their "Guide to the Literature of Chemistry," intended for the student in college as well as for the chemist of wider experience; this, however, is more of a reference book than a textbook. In "Chemical Publications" Mellon has presented a real textbook, based upon his undergraduate course in chemical literature.

The object of the book is stated to be three-fold: first, to sketch briefly the general trend of events giving rise to and accompanying the development of chemical publications; second, to present an outline of the present sources of published chemical information, with a consideration of the general nature of each class and of typical examples in the various classes; and third, to suggest certain exercises indicating possible laboratory work for class use.

The book opens with a discussion of original sources: periodicals, institutional publications (covering mainly Federal documents), patents and their literature, dissertations and manufacturers' bulletins. Then follows a discussion of the so-called secondary sources: abstract journals, review serials, bibliographies, general works of reference and textbooks.

This material, comprising the first eight chapters, covers in an abbreviated form the material previously covered by Crane and Patterson, but it is felt that it is presented in such a way as to be more useful to the group for which it is intended. The real purpose of the book will be found in the last two chapters, which discuss "Making Searches in Chemical Literature" and "Library Problems." After introducing the student to the methods of classification used by libraries, the card catalog and indexes, directions are given for making a short and an exhaustive search of the literature. Finally, there is presented a series of fourteen problems, sufficient for a semester of sixteen weeks. These are of increasing complexity, starting with data regarding a given journal, institutional publication or patent, then going to data regarding a given chemical, chemical system, apparatus or process and concluding with the preparation of a bibliography and a critical report.

The reviewer has had ample opportunity to observe the need of this kind of training for our chemical students. For example, many of the questions which come to the Research Information Service of the National Research Council could be answered by the inquirer by consulting the standard textbooks or the indexes of *Chemical Abstracts.* Another point which should be emphasized by the instructor in such a course is accuracy in literature citations. When one finds a bibliography with from ten to fifty per cent. of errors, one cannot but wonder at the accuracy of the body of the paper to which the bibliography is appended. While much of this is due to the inexcusable habit of copying citations from published papers without first verifying them, it in no way relieves the author of his responsibility.

Professor Mellon has presented a very helpful book and it is to be hoped that the appearance of this work may stimulate the chemical departments of many universities to introduce a course on "Chemical Literature" as a part of their regular curriculum.

CLARENCE J. WEST

Chemical Patents Index. A Comprehensive and Detailed Index of the Subject Matter of Specification and Claims of United States Patents and Patent Reissues Granted during the Decennial Period 1915–1924 Inclusive, Covering the Entire Field of Chemical Technology. By EDWARD CHAUNCEY WORDEN, FIRST. Ph.C., B.S., M.A., F.C.S., F.L.S. Volume I. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1927. 904 pp. 17 × 25 cm. Price, $25.00.

This is the first of five volumes which will contain a detailed and comprehensive index of the United States Patents during the decade 1915–1924. During this period 398,377 patents were issued, of which 22,882 dealt with some branch of chemical technology. 14,526 names are recorded as sole or joint inventors in these patents. The chemical patents were examined in detail and an index card prepared for every chemical substance or class or process mentioned. It is stated that in one extreme case 2756 cards were prepared from a single patent. The work will obviously be extremely useful to anyone who has to deal with chemical patents in any way. Its usefulness is, however, limited by the fact that it covers only a single decade. Therefore the index can supplement, but not replace, the older and more cumbersome method of making a patent search. Fortunately the author announces that he and his staff are now engaged in extending the work to cover the decade 1905–1914 and the period 1925–1926. It is to be hoped that the work will receive sufficient support to make possible its extension backward and forward.

It may be of interest to append the first dozen names of inventors in order of number of chemical patents issued during this decade, together with a few other well-known names: C. Ellis, 237; W. Snelling, 67; W. Lindsay, 47; S. Peacock, 47; A. Backhaus, 46; H. Dreyfus, 41; W. Kempton, 40; L. Barton, 39; R. Benner, 38; S. Carroll, 38; R. Price, 38; T. Edison, 37; L. Baekeland, 28; H. Howard, 27; H. Dow, 24; G. Claude, 20.

GRINNELL JONES

L'État Colloidal et l'Industrie. (The Colloidal State and Industry.) By W. KOPACZEWSKI, **M.D., Sc.D., Professor at l'Institut des Hautes Études, Belgium. Vol. II. Librairie Polytechnique. Ch. Béranger, 15 Rue des Saints Pères, Paris, France, 1927. viii + 344 pp. 68 figs. 16 × 25 cm. Price, fr. 70.**

Vol. I appeared in 1925, and in response to the criticism it drew that the treatment of many industries was summary, the author in his present preface points out that these books are meant to serve as a complement to existing technologies, supplying missing colloidal data.

Vol. II is divided into three parts: (1) applications dealing with the mechanical properties of colloids (including decantation, filtration, centrifugation, ultrafiltration, dialysis, diffusion, adsorption, catalysis and its applications); (2) applications of the electrical properties of colloids (including sorption and its applications and electrophoresis); **(3)** equilibrium conditions of the colloidal state (including stabilization and labilization of hydrosols, swelling and syneresis of gels). The indexes and tables of contents of both volumes are included, and each chapter is followed by a bibliography, which does not, however, enable the reader to locate the source of each statement directly.

The author has compressed into this book a large amount of useful information and his references indicate that he has not confined his wide reading within national or linguistic lines, so that there is hardly anyone who will not get much good of it. All told, however, one receives the impression that some of the information comes directly from patents, books or journal articles, and expresses points of view rather than commercially and technically accepted procedure. Few will agree to placing the lower colloidal limit or size at 20 $m\mu$; but then, one does not have to agree with everything an author says to profit by his labors.

JEROME ALEXANDER

Pharmaceutical and Medical Chemistry. By SAMUEL P. SADTLER, Ph.D., LL.D., late Professor Emeritus of Chemistry in the Philadelphia College of Pharmacy, Virgil Coblentz, Ph.D., F.C.S., Professor Emeritus of Chemistry and Physics in the Department of Pharmacy of Columbia University, and Jeannot Hostmann, Ph.G., late Associate Professor of Chemistry and Director of the Analytical Laboratory in the Department of Pharmacy of Columbia University. Sixth edition, revised and rewritten by Freeman P. Stroup, Ph.M., Professor of General Chemistry, Philadelphia College of Pharmacy and Science. J. B. Lippincott Company, Philadelphia and London. **15** X **23.5** cm.

As stated in the preface to the present edition, "The appearance of the United States Pharmacopeia X, the National Formulary V, and the 1926 edition of New and Non-official Remedies has made it essential that a new edition of this book be prepared. Besides, many manufacturing chemical processes have undergone change and many new substances have come into more or less general medicinal and pharmaceutical use in recent years." A comparison of past editions with the present one reveals no material change in the general character of the book, although the authors have striven to bring the text up to date and to amplify certain portions obviously needing such attention. Revision of both the inorganic and organic sections has been thoroughly effected. The section on chemical physics is omitted from the present edition owing to the fact that in most college courses in pharmacy today more elaborate courses in physics are available than formerly. This saving in space is taken advantage of by the introduction of entirely new matter of a purely chemical character, as also by materially enlarging the index, thus rendering the present edition more desirable both as a textbook and reference work. Serious errors are few as will be readily apparent to the reader. A typographical error has, however, apparently crept into the periodic system of the elements, p. 208, Period E, Column V, Se should read Sb.

W. O. EMERY

Glycerol and the Glycols. Production, Properties and Analyses. By JAMES W. LAWRIE, Ph.D., Research Chemist, E. I. DuPont de Nemours and Co. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., **419** Fourth Avenue, New York City, **1928.** 447 pp. 81 figs. **15.5** × **23.5** cm. Price **$9.50.**

This book is an interesting and valuable addition to our knowledge of industrial aliphatic chemistry, containing as it does a very thorough review of the subject and many new and otherwise inaccessible data.

The first four chapters give a review of the sources, methods of production and manufacture of glycerol from soap lyes.

In Chapter V the synthesis of glycerol by fermentation is described at length and in Chapter VI the physical properties and constants of glycerol and its aqueous solution are given. For the latter it is evident that the author has drawn freely on the valuable data in the DuPont files, which are otherwise inaccessible.

The chemistry and reactions of glycerol, its detection, analysis, specifications and commercial utilization are discussed in a thorough manner, while chapters on the manufacture of glycerol trinitrate, glycol dinitrate and the methods of production of the glycols also contain much valuable information.

While the text is printed in the customary clear type the same cannot be said of the numbering of the footnotes.

The subject matter has been carefully corrected, to judge from the few misspelled words noted, *e.* g., p. 206, hypochlorus; p. 224, pyrocatechic, isophorn; p. 314, glycerite; p. 348, labil; p. 388, difficient; p. 371, internals.

Formula II on p. 387 is incorrectly given, as is also the formula for ethylene on p. 363. Table 113 on p. 381 is incorrectly given as Table 112. A few other points calling for comment are the following: The statement (p. 44) that propylene chlorohydrin can be hydrolyzed to glycerol is obviously incorrect. The same remark also applies to the statement that glycerol is a triose. The boiling point of di-iso-amylin calls for correction, as well as the spelling of the word. It would seem advisable to insert in a footnote to Table 113 the significance of the letters used. The term "artificially" (p. 220) should be replaced by "synthetically."

In Table 98 the melting points of the two forms of the trinitrate are given as 2.2 and 12.2" and in Table 99 as 2.5 and 13.5". The values obtained by the reviewer and co-worker in a carefully conducted research were 2.0 and 13.2" and so far as is known represent accurate data.

The author (p. 212) gives the number of theoretical oxidation products of glycerol as eleven but overlooks hydroxymalonic acid (tartronic acid).

The latent heat of fusion is given in a clear-cut statement (p. 348) as 23.1 calories per gram, while on p. 391 attention is drawn to the probable incorrectness of the figures by quoting the same author's own attitude.

This value was carefully determined by the reviewer and co-worker and there is no doubt as to the inaccuracy of Nauckhoff's figures. As given in the text it would seem that the doubt is on the side of Hibbert and Fuller's results. The description of the apparatus, Fig. 70, p. 359, does not correspond with the text; at least it is difficult to recognize in the sketch a graduated centrifuge tube of the dimensions given.

One point which calls for criticism (and for which the editors of these Monographs must also be held responsible) is the careless use of the terms nitro and nitrate. The author repeatedly speaks of nitro glycerol and nitro glycols when obviously glycerol and glycol nitrates are meant. Thus nearly all of the names used in Table 99, and in much of the text, are scientifically inaccurate and misleading. It is to be hoped that this nomenclature will be carefully revised in any subsequent edition.

The author's views on the future of glycerol and the possibility of its synthesis are of interest. The fermentation process would seem to hold, at present, far greater possibilities than the synthesis from petroleum.

In tabulating the various factors which have led to the recent slump in the price of glycerol the most important is omitted, namely, the commercial development of the manufacture of ethylene glycol at a competitive price.

In the opinion of the reviewer, who has devoted a number of years of his scientific career to the possibility of the synthesis of glycerol and glycols, there are few basic organic raw materials which offer more wonderful possibilities than glycerol.

The makers of this product need not necessarily be at all pessimistic about its future, for if they are willing to spend on scientific and technical research only a fraction of the total sum expended on the commercial development of synthetic glycols, there is reason to believe that they will find other more highly profitable outlets and thus render themselves more independent of its present restricted commercial application.

Dr. Lawrie's book can be strongly recommended as a valuable and authoritative work to all interested in the future development of industrial organic chemistry.

The dedication of it to Professor Julius Stieglitz is an admirable and charming tribute to an investigator who has contributed much to the advancement of organic chemistry.

HAROLD HIBBERT

The Journal of the American Chemical Society

VOL. 51 APRIL, 1929 No. 4

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 185]

THE OXIDATION OF BENZOYL-ORTHO-TOLUIDINE AT A BENZENE–WATER INTERFACE WITH SPECIAL REFERENCE TO THE TEMPERATURE COEFFICIENT OF THE REACTION RATE

BY LOUIS S. KASSEL[1] AND NORWOOD K. SCHAFFER

RECEIVED JULY 9, 1928 PUBLISHED APRIL 5, 1929

In a recent paper, R. P. Bell[2] has reported some reaction rate measurements for the system aqueous potassium permanganate–benzoyl-o-toluidine dissolved in benzene. Oxidation occurs at the interface and the solubility relations at 25°, according to Bell, are such that an appreciable amount of homogeneous oxidation of A[3] cannot occur. Bell finds that the rate of this reaction is independent of the rate of stirring of the benzene layer over a four-fold range, and that the 10° temperature coefficient for the range 15–25° is 13, corresponding to an energy of activation of 43,700 cal. He finds that the reaction is of the first order with respect to the permanganate, and that the rate increases with the concentration of *A* for low concentrations; but becomes independent of concentration at about 5–6 grams/liter. This suggests the formation of a saturated film at this concentration, and since the same conclusion is reached from an application of the Gibbs-Helmholtz equation to the interfacial tensions for the system water–benzene–A, this conclusion is probably correct. The permanganate is almost certainly negatively adsorbed and the reaction may well occur upon the impact of permanganate ions on the adsorbed film of A. It is this mechanism which Bell has proposed.

Our attention was directed to this work by the extremely large temperature coefficient which Bell found. Few reactions have temperature coefficients greater than 4, and none, so far as we are aware, in excess of 7, at temperatures where their rates are appreciable. No mechanism which we could construct was capable of accounting for the magnitude of the observed rate; the discrepancy in all cases amounted to a factor of at least

---

[1] National Research Fellow in Chemistry.

[2] Bell, *J. Phys. Chem.*, 32, 882 (1928).

[3] Hereafter, for brevity, benzoyl-*o*-toluidine will be designated by A, and benzoyl anthranilic acid, one of the oxidation products, by B.

10^{20}. It thus seemed that, if this value 43,700 calories was in any way related to an actual energy associated with the reaction, some new ideas would have to be introduced into reaction rate theory to account for the speed of this reaction. Before this was attempted, however, it appeared desirable to verify the experimental results, and this we have attempted to do. Our work disagrees with that of Bell in three particulars.

1. Bell gives a list of desirable characteristics for an interfacial reaction, to which the one selected presumably conforms. One of these characteristics is that no solid should separate out. He states especially that although B is rather insoluble in benzene and but slightly soluble in water, his rates apply to the initial part of each run, during which it all remained in solution. He makes no statement about manganese dioxide, but by implication one would suppose that it is not formed. Since the reaction is started in a neutral solution and since this solution can scarcely avoid becoming alkaline as the reaction proceeds,[4] the formation and precipitation of manganese dioxide is to be expected. It actually occurred in all of our experiments, and we cannot see how it could have been absent in Bell's.[5]
2. Bell varied the rate of stirring of the benzene layer by a factor of 4, keeping the rate of stirring in the water layer constant, and found no change in the rate. He therefore concluded that the rate of reaction was independent of the rate of stirring. We found that when the rate of stirring in both layers was increased, the rate of reaction increased markedly.
3. We did not verify Bell's value of 13 for the temperature coefficient, but instead found a value of about 2.

Experimental Part

A was prepared by benzoylation of technical o-toluidine in benzene solution. The resulting material was filtered hot and A separated out upon cooling. It was then recrystallized from benzene. Three separate preparations were used during the work. The first (Sample I) was not washed with hydrochloric acid at any stage. Sample II was washed with dilute hydrochloric acid and then with water after recrystallization and Sample III with the same reagents before recrystallization. Samples I and II melted at 139–140° and Sample III at 142°. The value given by "International Critical Tables" is 143°.

The reaction was carried out in a five-liter bottle of brown glass. The area of the

---

[4] The equation $2KMnO_4 + A \longrightarrow 2MnO_2 + B + 2KOH$ certainly would lead to increased alkalinity. So would $6\ KMnO_4 + 5A + 4H_2O \longrightarrow 6Mn(OH)_3 + 5B + 6KOH$. Any further reaction which took place could only increase the alkalinity.

[5] Since the submission of this paper, we have been informed by Bell (private communication) that in the initial parts of his runs the manganese dioxide did not separate out, but that on standing this did take place. It appears that it is formed as a colloid. Our own observations on this point are incomplete, since we could not examine the surface closely until after the reaction was stopped, but we have some reason to believe that in our experiments also the initial stage does not involve precipitation. though the colloid does not appear to have been as stable as in Bell's experiments.

interface was 220 cm.^{2}. A single stirrer was used for both solutions, with three paddles in the water layer and one in the benzene. A protecting tube of about 5 cm. length surrounded the portion of the stirrer which passed through the interface, so that the disturbance produced would be confined to a small region, but the alignment was good enough so that even that small part of the interface was not noticeably agitated. The paddles were perfectly straight horizontal rods, about 8 mm. in diameter and 20 mm. long. The three paddles in the water layer were mounted at angular intervals of 120° and vertical intervals of 10 mm. The chief reason for the rather inefficient design was that otherwise it would have been almost impossible to give even a crude idea of the amount of stirring produced.

The course of the reaction was followed by withdrawing 10-cc. samples of the permanganate solution from time to time and titrating with freshly prepared ferrous ammonium sulfate solution; this seemed preferable to the oxalic acid which Bell used, since it was unnecessary to heat the solution during the titration and the chance of reaction between B and the permanganate in the hot acid solution was thus avoided. The pipet with which the solution was withdrawn passed through a protecting tube which contained no benzene layer; since almost all of the manganese dioxide collected at the interface, this made the sampling more reliable than it would have been otherwise.

The thermostatic regulation was entirely adequate. Fluctuations as great as 0.05" did not occur.

Altogether 20 runs were made. The first five were preliminary and since they were made with a different stirrer or in a different reaction vessel than the others the results will not be reported. Run 6 was made with 1400 cc. of benzene solution, containing 5.36 grams/liter of A, and 1750 cc. of about 0.035 N permanganate. All of the following runs were made with 1000 cc. of benzene containing 6 g. of A, and 1750 cc. of about 0.005 N permanganate. Runs 6–10 were made at 25.0° using Sample I. In each of these runs one or more changes was made in the rate of stirring during the run, and with a single exception each change resulted in a perfectly definite change in the rate of reaction. The exception was in run 9, which showed no abrupt change when the rate of stirring was increased from about 20 r.p.m. to 80; the measurements were not continued a sufficiently great time after the change to make the results definite and the run could never be duplicated. In general it may be said that at rates of stirring of 80 or more the results are reproducible with quite fair accuracy, but that at lower rates they are erratic. For example, in run 4, with a different stirrer, no reaction was observed in five hours at 20 r.p.m., nor in one hour at 33, but a rapid reaction set in at 160; in run 9, as has been said, a slow reaction occurred at 20 r.p.m.; in run 10 no reaction had occurred after eight hours at speeds of 10–45 r.p.m.; run 11, with Sample II, gave reaction at 20–50 r.p.m., while run 12, with the same sample but at 27.9°, showed no reaction in three hours at 20–40 r p.m. Since the time available for these experiments was limited, we were forced to abandon this part of the investigation without reaching a definite conclusion as to the relation between the rate of reaction and the rate of stirring at rates less than 50 r.p.m. Between 50 and 250 r.p.m., however, there is a very definite and marked dependence on the rate of stirring. This is shown by Pig. 1, in which the observed rates in runs 6, 7, 9 and 10 (run 8 gave about 100 times the normal rate, but it also showed dependence on the stirring) are plotted against the rate of stirring. The rates are given in moles of permanganate per hour per cm.^{2} of surface per unit molarity. The general trend of the points is quite obvious except at low rates, The rather considerable scattering is attributable mainly to two causes; it was not always possible to keep the rate of stirring quite constant, and some of the abscissas represent mean values which may not be accurate. Most of the points at higher rates were obtained from the later parts of runs, when varying amounts of manganese dioxide were present; this, or some other reaction product, appears to have a poisoning effect on the surface, so that rates which were not obtained under **exactly** corresponding conditions should not be expected to agree perfectly. The best evidence that between **50** and **250** r.p.m. the rate does depend on the stirring is obtained from the single runs. The complete data for run **7,** which is fairly typical, are shown in **Fig. 2.** We did not work at greater rates than **250** r.p.m. because at that rate the stirring had become rather violent; it is scarcely possible to suppose that such agitation is not much more than is needed to keep a fresh supply of reactants at the surface and the increase in rate which occurs with increased stirring in this region is probably due to a breakdown in the oriented absorption of *A*, giving a condition more favorable to reaction, or to incipient emulsification, with a consequent increase in the area of the interface; that this last suggestion is not unreasonable follows from the fact that visible emulsification occurs at rates of about **500** r.p.m.

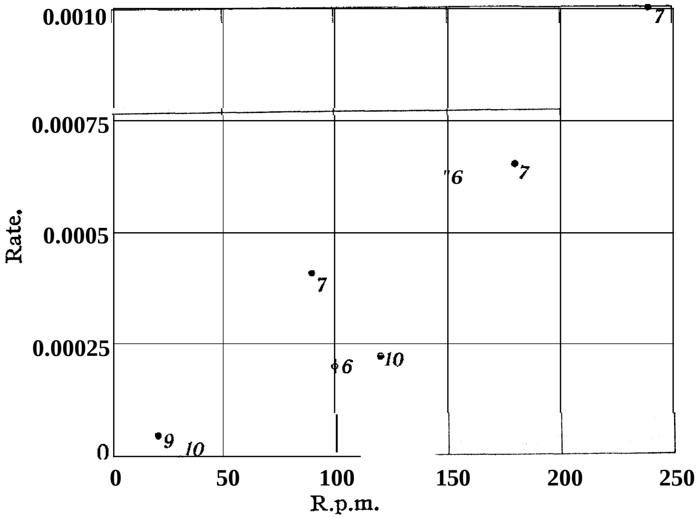


Fig. **1.**

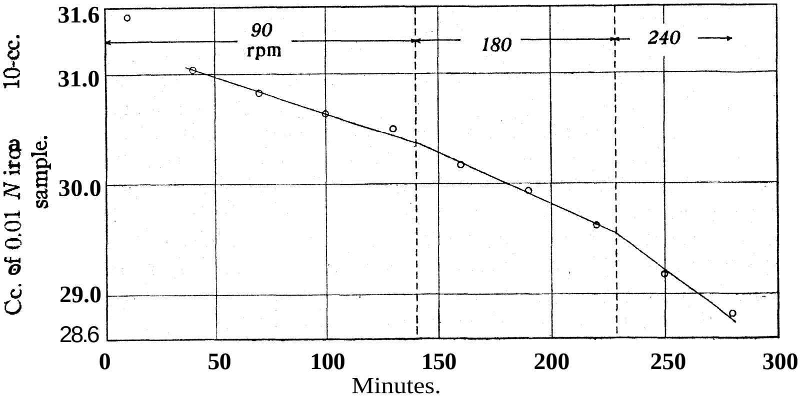


Fig. 2.

The remaining runs were devoted to a determination of the temperature coefficient of the reaction rate at about **120** r.p.m. Runs 13–16 were made with Sample II and runs **17–20** with Sample III. The temperature range of the former series was only 30–40° and the stirring was somewhat erratic. The results confirm those of the latter series but cannot be regarded as very reliable. Runs **17–20** were all very good and the technique of regulating the stirrer had been mastered by then. The sample used was the best of the three; it reacted more slowly than did Sample II, and the rates, therefore, apply to the initial part of the reaction when only a small amount of manganese dioxide was present. The separate titrations with few exceptions were in good agreement and the determination of the rate from the slope of a straight line drawn through the experimental points was subject to an uncertainty of not more than 5%. The complete data for run 18 are shown in Fig. **3,** and the results for the entire series are listed in Table I.

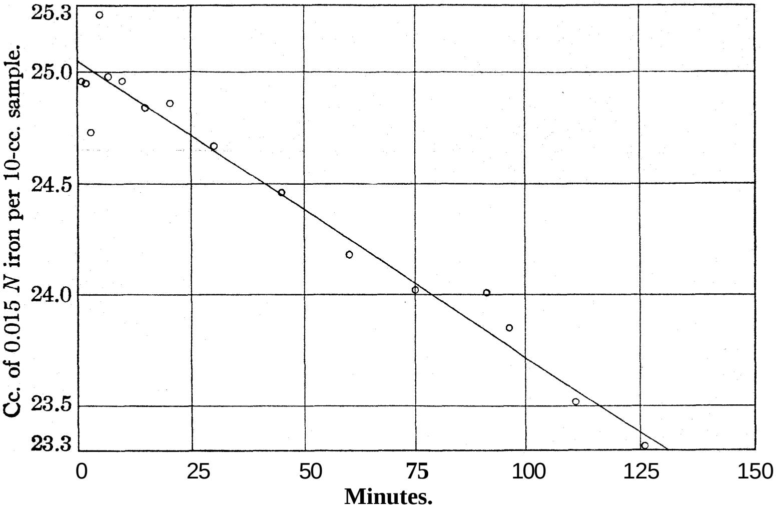


Fig. 3.

TABLE I

RESULTS FOR THE SERIES

Run number	17	18	19	20
Temperature, °C.	25.6	45.3	35.16	15.3
k	0.00025	0.00120	0.00052	0.000126

In this table k is the number of moles of permanganate reduced per hour per cm.^{2} of surface per unit molarity of the permanganate, with 6 g./liter of A in the benzene solution, at **120** r.p.m. with the stirrer described.

In Fig. 4 is shown a plot of ln k against $1/T$ for these values. The four points lie on a smooth curve which, however, is not a straight line. The curvature is not great but is far from negligible, as a calculation of the energy of activation E_0 for various intervals shows.

TABLE II

VALUES OF E_0

Temperature interval, °C.	15.3–25.6	25.6–35.15	35.15–45.3
E_0	11,500	14,100	16,200

These values are all subject to a correction of $RT/2$ if the reaction is bimolecular, but this is in any case negligible.

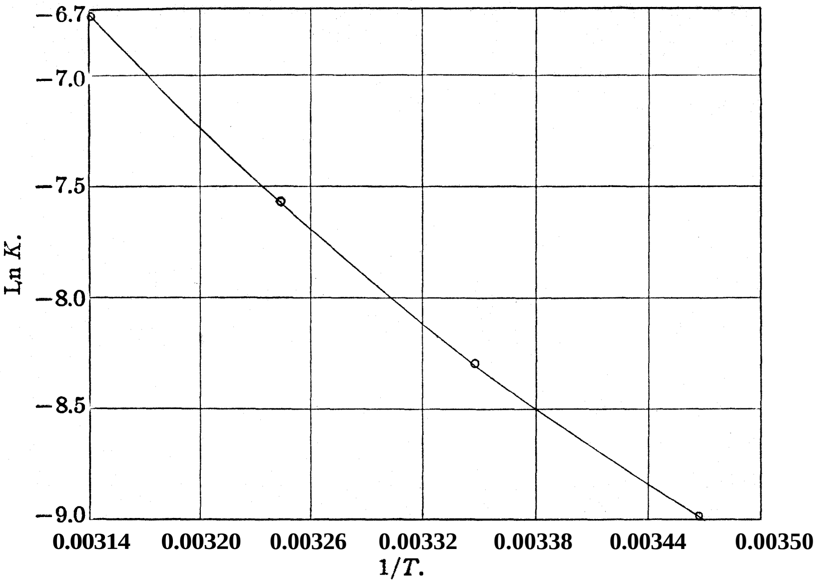


Fig. 4.

Discussion

If this trend in the value of E_0 is real, as we believe it to be, there are a number of possible explanations for it. The reaction product, B, is not perfectly stable to permanganate, and there may be a slow but appreciable homogeneous reaction occurring, particularly at the higher temperatures. This could result in a trend of the sort observed if the homogeneous reaction had the larger temperature coefficient. Or, since A is distinctly soluble in boiling water, it may not be quite insoluble at 35–45°. Thus, there may be a certain amount of homogeneous oxidation of A in addition to the main heterogeneous part of the reaction. This would lead to a trend of the type observed, regardless of which reaction had the greater temperature coefficient, but it would seem very likely, if this explanation is correct, that the larger one belongs to the homogeneous reaction, first because that is the normal situation, and second because in this case the temperature coefficient for the homogeneous reaction would include the temperature coefficient of solubility. Then the energy of activation for the interfacial reaction would be less than 11,500, and that for the homogeneous reaction greater than 16,200. Other explanations for this trend in E_0 are possible; in fact, any two or more reactions, either simultaneous or successive, both leading to a reduction of permanganate, are capable of accounting for it.

It is not possible from the results of our work to assert definitely what the cause of the disagreement between our results and those of Bell is, but we believe that the following reason will probably account for it. Bell says (p. 883), "One preparation was recrystallized from alcohol and one from benzene. . . . Both were therefore considered pure and were used indifferently in the subsequent work." The first series of Bell's runs (Runs 5–16) is devoted to a determination of the dependence of the reaction rate on the concentrations. The first three of these, taken alone, show the reaction to be first order with respect to the permanganate; the last six, made at approximately constant permanganate concentration, give a smooth curve when the rate is plotted against the concentration of A. The velocity read from the curve for 4.55 g./liter of A is 3.3 cc./hour. The first three runs of the series were made at 4.55 g./liter of A, and when corrected to the same permanganate concentration as the other six give, in the same units, a rate of 0.56 cc./hour. The discrepancy, a factor of 6, is scarcely assignable to experimental error in view of the good agreement within each of the two groups. Bell does not mention this disagreement at all; since our own three samples showed considerable differences in rate, we consider it probable that the same is true of the two Bell used, and that the first three runs of this series were made with the less active sample. It is worth noticing that if his temperature coefficient, 13, be divided by this ratio, 3.3/0.56, the result is 2.2 in very good agreement with our own value of 2.0 for the same temperature interval. If this suggestion as to the cause of his error is correct, then he must have made Runs 5, 7, 8 of Series 1 and all those of Series 3 with a single sample, the less active one; and must have made the remaining runs of Series 1 and all those of Series 2 with the more active sample.[6]

With regard to the actual nature of the catalyst responsible for the varying activity of the different preparations, we have no suggestion to

---

[6] Bell has informed us that the explanation we suggest is not acceptable. It seems that the runs for which the reported concentration of *A* was 4.55 g./liter were made at an actual concentration of 1.55 g./liter. This removes the factor of six pointed out above. Furthermore, all the runs on which the temperature coefficient was based were made with a single sample. Bell is willing, however, to accept our value for the temperature coefficient, since his study of this quantity was a minor point in his investigation. We wish to emphasize that the main thesis of his work, the verification of the Gibbs–Helmholtz equation, is not affected by our work.

make. Of our three samples, I was about twice as active as III and II 5–7 times as active.

It may be worth while to repeat the calculation which Bell has given for the fraction of fruitful collisions of permanganate ions at the interface. This is necessarily based on the unlikely assumption that the ions may be treated as a perfect gas. It is found that at 25°, making this assumption, 2.07×10^4 moles would strike per cm.^{2} per hour per unit molarity, and of these 0.00025 moles would react. The fraction of fruitful collisions is, therefore, 1.2×10^{-8}, about one-tenth that Bell found; in the absence of knowledge as to the rate of stirring that he used this is not very significant, though it points to a somewhat lower rate for our Sample III than for either of his. If we put $1.2 \times 10^{-8} = e^{-E_0/RT}$ and solve for E_0, we get 10,900 calories. This value is not very significant. The calculated number of molecules striking is quite possibly in error by a large factor, due to negative adsorption among other causes; the chances are that it is too large. This would mean that the true fraction of fruitful collisions is greater than that calculated, and the corresponding true value of E_0 would be smaller. However, the direct calculation of E_0 in this way is rather naive. It has been suspected for a long time, and the great mass of experimental data of Hinshelwood and others show it to be so, that the rate of a bimolecular gas reaction is calculable by multiplication of the number of collisions with the factor $e^{-E_0/RT}$; but there is no certainty that the actual mechanism of the reaction considered here is bimolecular (for example, it might involve the unimolecular breakdown of a complex formed between A and a permanganate ion) and furthermore the work of Norrish and Smith[7] shows that for reactions occurring in solution it is necessary to introduce a probability factor P, which may be very small. The omission of this factor, if it should be present, would make the calculated value of E_0 too large. There are thus at least two sources of error, both tending to make the calculated value of E_0 too large, so that the true value is probably less than 10,900 by a considerable amount, although some unsuspected error in the other direction may change this. The value with which this calculated quantity is to be compared is also uncertain. If, as has been said was possible, the trend in the observed temperature coefficient is due to two reactions occurring together, that with the lower temperature coefficient being heterogeneous, then the energy of activation for the heterogeneous reaction is less than 11,500. In fact, on this basis, we should be justified in applying the $RT/2$ correction mentioned before and saying that it was less than 11,200. It is quite possible for a number less than 10,900 to equal a number less than 11,200, but this possibility does not lend any weight to the vast number of assumptions made in arriving at these figures. There is no large obvious discrepancy,

---

[7] Norrish and Smith, *J. Chem. Soc.*, **1928,** 129.

such as Bell's work appeared to involve, but more than that cannot be said. It is, of course, needless to mention that the close agreement between the numbers 10,900 and 11,200 is to be regarded as a coincidence without significance. There are several other causes which contribute to the uncertainty of the foregoing calculations. Among these are a possible variation of the concentration of the absorbed film of A with the temperature and the effect of the catalyst. It would be possible to clear up some of these points by further experimental work, but many of them seem destined to remain obscure unless information can be obtained from other measurements than those of reaction rates.

Conclusion

The general impression given by Bell's experimental results is that his work is reliable. On the whole his data are more consistent than our own. We therefore have felt safe in accepting, without verification, his results on the order of the reaction. His interpretation of the main reaction as being due to collisions of permanganate ions on the adsorbed film of A is inherently reasonable, and is not in disagreement with the very uncertain calculations of the last section. There does not seem to us, however, to be any certainty that it is correct. The trend in the temperature coefficient which we found probably means that there is some additional reaction occurring, but it is not possible to assert anything as to its nature. Much could be done by varying the depth of the aqueous layer, keeping other conditions constant. If the disturbing reaction is the subsequent oxidation of B homogeneously, this should change the disturbance and the main reaction by the same factor, leaving their ratio unchanged, while if there is a homogeneous oxidation of A it would increase in importance with the depth of the layer. Also, of course, the homogeneous oxidation of A could be increased, if it occurs, by increasing the concentration of A, best at a fairly high temperature. It should be remembered too that none of the existing derivations of the equation $(d \ln k/dT) = E_0/RT^2$ is directly applicable to a system in which the rate depends on the stirring, and that possibly the trend in the value of E_0 is normal. It does not seem to us, however, that the reaction is one which would repay further study; its twofold dependence on stirring and on an unknown catalyst make it rather unpromising from **a** theoretical standpoint, and, therefore, we do not intend to study the system further.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Summary

1. The oxidation of benzoyl-o-toluidine by permanganate at a benzene–water interface is dependent upon the rate of stirring and upon the presence of some unknown catalyst.

2. The temperature coefficient of this rate does not appear to be 13, as Bell reported, but, when runs under comparable conditions are made, is about 2. It increases somewhat with the temperature, indicating that more than one reaction is occurring.

3. The mechanism suggested by Bell, impact of permanganate ions on an adsorbed film of benzoyl-o-toluidine, does not disagree with the data, but it is impossible to make any but the crudest sort of verification. Other mechanisms are possible.

BERKELEY AND PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 186]

A TEST OF THE RADIATION HYPOTHESIS OF CHEMICAL REACTION[1]

BY WILLIAM URE[2] AND RICHARD C. TOLMAN

RECEIVED JULY 17, 1928 PUBLISHED APRIL 5, 1929

The viewpoint that thermal unimolecular reactions are to be considered as photochemical reactions with the activating frequencies lying in the infra-red region should be susceptible of experimental test by subjecting a system to radiation from an outside source and determining whether or not the thermal reaction rate is thereby increased. The difficulties in such an experiment arise from two sources. First, there is the necessity of obtaining a high intensity of infra-red radiation, without at the same time raising the temperature of the reacting substance to such a point that the normal thermal rate is the preponderating effect. In the second place, the extreme opacity of almost all substances to all but the shortest of infra-red rays makes it difficult to find a window that will permit a high intensity over the wide range of frequencies which may be important in activating the molecules. For since we do not know in what part of the infra-red spectrum the activating frequencies might lie, a conclusive. test of the hypothesis should involve the use of all frequencies which are present to an appreciable extent in a hohlraum at the thermal reacting temperature.

Daniels[3] has shown that over a considerable range of frequencies the unimolecular rate of decomposition of N_2O_5 is not appreciably affected by radiation. In the present experiments the effect of infra-red radiation on the rate of racemization of d-pinene in the liquid state was studied.

---

[1] Presented before the regional meeting of the Pacific Division of the American Association for the Advancement of Science, June, 1928.

[2] This is part of a thesis submitted by William Ure to the Division of Chemistry, California Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Daniels, THIS JOURNAL, 48,607 (1926).

This reaction has been shown by Smith[4] to be unimolecular in the gas phase, in the liquid and in solution in various organic solvents. During the progress of the work Lewis and Mayer[5] and Mayer[6] published the results of a research also dealing with the activation of pinene by infra-red radiation. The conditions of their experiment were such that the molecules in the form of a molecular ray were subjected to an intense field of radiation for a very short length of time. Their method had the advantage of doing away with the necessity for any window and of eliminating collisions so that any effect noticed would be due to radiation. No racemization was detected.

It is to be observed, however, that in experiments in which the reacting substance is at a temperature much below that at which the thermal rate is appreciable, practically all of the molecules are in energy states which are very low compared to that of the energy of activation. Hence, since the energy per quantum of infra-red radiation is also small, only a few molecules will be in states from which they can become activated by absorption of a quantum, and thus the increase in rate brought about by the radiation may be unobservably small. This point will be considered in more detail later. For this reason the present experiments are of interest, since they differ from the work of Lewis and Mayer in that pinene was subjected to radiation while at a temperature at which the thermal reaction was just appreciable. The density of radiation in the shorter infrared has been increased by a large factor over that which prevails in a hohlraum at the reacting temperature of pinene. Thus if radiation of the frequencies over which it was possible thus to increase the density was active, a large increase in the already measurable rate should have been observed. This was not found and within the limits of error no increase in rate was observed.

Experimental Determination of the Rates

Apparatus.—The liquid pinene was contained in a vessel having a large window of very thin mica, which is highly transparent to the near infra-red, and was subjected to an intense beam of radiation from the open end of a cylindrical furnace kept at 850° which was situated just below the window. The vessel was cooled by air-blasts and the temperature of the liquid was maintained in the neighborhood of the boiling point, 156°.

The experimental arrangement is shown in Fig. 1. The reaction vessel A was a hemispherical glass vessel 5 cm. in diameter, the rim of which was flared out and ground flat, the mica sheet **0.04** mm. thick being clamped in place between two brass rings and a tight seal ensured by inserting cork gaskets. The cork was found to have no effect on pinene over a considerable period of operation.

It was found necessary to conduct the experiments in an atmosphere of nitrogen, since considerable oxidation of the pinene was found to take place in the presence of

---

[4] Smith, THIS JOURNAL, 49, **43** (1927).

[5] Lewis and Mayer, ***Proc. Nat. Acad. Sci.***, 13, 8, 623 (1927).

[6] Mayer, THIS JOURNAL, 49, **3033** (1927).

air during the length of time and at the temperature necessary for the runs, and the construction of the reaction vessel made evacuation impossible. The reaction vessel was accordingly connected through the upright condenser B with a 5-liter bottle filled with dry nitrogen, and arrangement also made to bubble nitrogen through the liquid from the side-tube C. A tube D leading to within a few millimeters of the mica window and connected to a small reservoir E rendered filling and emptying the vessel an easy matter. The small reflux condenser B prevented the loss of pinene during the run. At F a thermocouple was inserted through a thin glass tube.

The radiator consisted of a cylindrical alundum tube 5 cm. in inside diameter and 25 cm. long, closed at the bottom end and wound with chromel wire No. 22 in the following manner. The tube was first completely wound in a spiral groove provided. The whole winding was then covered with a layer of "insalute" cement and the winding continued back over the upper half of the tube, giving a total length of about 65 ft. of wire. This allowed the upper end of the tube, which was left open, to attain more nearly the temperature of the lower end, which was closed and had better heat insulation. The lower end was closed by a disk of asbestos board, on the inside of which was attached a small helical coil containing about 6 ft. of No. 22 chromel wire. This was covered with a layer of "insalute" which then formed part of the inner wall of the furnace. The whole furnace was packed in asbestos, leaving the top open, except that this end was covered by a mica window 0.025 mm. thick to minimize cooling. A thermocouple junction was embedded in the wall of the furnace at approximately half-way along the tube. The interior walls of the furnace were coated with a mixture of powdered copper oxide with a small amount of "insalute" as a binder, thus giving a surface of a high degree of "blackness."[7] The furnace was operated at approximately 115 volts, A.C., and 2.2 amperes, the current being adjustable by hand in the body winding and in the end helix separately.

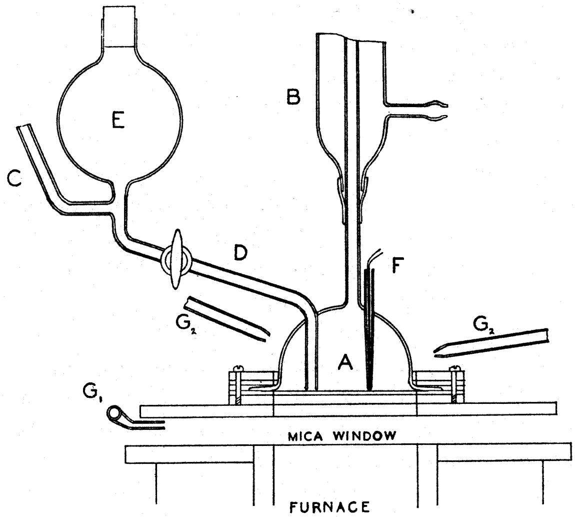


Fig. 1.

The reaction was followed by observing the optical rotation of the liquid, using a

---

[7] See Coblentz, "Investigations of Infra-red Spectra," *Carnegie Institution Publication Number 97, 1908,* Part VII, p. 119.

polariscope reading to 0.01'. A 10-cm. tube was used for convenience in handling small quantities of liquid. It had a capacity of about 12 cc. and was enclosed in a water jacket through which water at 25° was pumped from a thermostat during measurements.

Material Used.—The pinene was obtained from Kahlbaum. It had an initial rotation at 25° (10-cm. tube) of +45.3° and was slightly yellowish in color. Fractionation under reduced pressure gave a colorless liquid of rotation +46.2 to +46.6° and $d_{4^\circ}^{25^\circ}$ of 0.857 to 0.855. Cildermeister and Hoffmann[8] record for *d*-α-pinene from Grecian turpentine $d_4^{25} = 0.854$. The thermal rate of samples of the same pinene was observed in the gas phase by a method similar to that used by Smith." The temperature was that of boiling *p*-nitrotoluene (237") and the values of k_1 obtained were 3.03×10^{-3} and 2.91×10^{-3} min.$^{-1}$, being in good agreement with Smith's value of 3.07×10^{-3} min.$^{-1}$.

Experiments.—About 20 cc. of pinene was placed in the reaction vessel, forming a layer over the mica window 1.2–1.4 cm. thick. A stream of dried nitrogen was then bubbled through the liquid through the tube C for about ten minutes to displace all of the air in the vessel. The stopcock was then closed and the system connected to the nitrogen reservoir. The furnace was moved up into a position with the open end 1.7 cm. from the reaction vessel window. A blast of air was passed between the two windows from the fan-shaped tube G_1 and two jets of air G_2 directed on the upper side of the reaction vessel for the purpose of regulating the temperature of the liquid. The temperature was allowed to rise to the neighborhood of the boiling point. The liquid was not allowed to boil vigorously in case sudden increase in pressure might rupture the window. Runs were carried on for from four to eight hours, the temperature of the liquid and that of the furnace being taken at frequent intervals. The current to the furnace was kept about 2.2 amperes by a hand-operated rheostat. The liquid varied in temperature 4–6° during a run and the furnace temperature 10–15°. At the expiration of a run the furnace was removed and the liquid cooled to room temperature by the air blast. It was then expelled into the reservoir E and removed from there to the polariscope tube.

Results.—The results of four experiments are shown in Table I. The fifth and sixth columns give the average of a number of polariscope readings, taken before and after the run, respectively, individual readings being reproducible to 0.03'. The seventh column shows the difference; it is to be noted that a slight decrease was observed in all four runs but only in the last two does this become greater than the error of measurement. That this decrease is due to the thermal reaction taking place at the temperature of the liquid is shown by the figures of Col. 9, which are calculated values of the decrease for the thermal reaction at the average temperatures given. The constants at these temperatures, which are shown in Col. 8, were obtained by determining the rate at the boiling point, 156°, and then extrapolating down over the small temperature interval involved using Smith's value of the heat of activation, 43,710 cal./mole. The rate at the boiling point was determined experimentally by keeping pinene at 156° in an atmosphere of nitrogen for periods of twenty-four hours. The rate thus found, $k_1 = 1.90$ X 10^{-6} min.$^{-1}$, was about

---

[8] Gildermeister and Hoffmann, "Die atherischen Öle," Schimmel and Co., Leipzig, 1910, Vol. I, p 305

50% higher than that obtained by a direct extrapolation of Smith's data using his rate for the liquid at 184.6°.

TABLE I

RESULTS OF EXPERIMENTS

Run	Furnace temp., °C.	Liquid temp., °C.	Time, min.	α_1	α_2	A	$k_1 \times 10^6$ (min.$^{-1}$)	$\Delta\alpha$ (calcd.)
1	792–823	143	260	$46.74"	+46.73°	−0.01°	0.383	−0.01"
3	837–844	152	245	$46.71"	+46.70°	− .01°	1.17	− .03°
4	846–857	154	318	+46.70°	+46.65°	− .05°	1.50	− .04°
5	844–858	150	500	+46.64°	+46.60°	− .04°	0.918	− .04°

Determination of the Intensity of the Radiation

The Effective Temperature of Furnace.—In order to determine the intensity of the radiation available for activation, it was first necessary to obtain a check on the effective black-body temperature of the furnace. This was done in the following way.

The flux of radiant energy coming from the furnace was determined after the method of Daniels[3] by absorbing the energy in a solution of copper chloride and measuring the rise in temperature produced. Coblentz[9] has shown that a 2-cm. layer of 2.5% cupric chloride solution will absorb practically all of the energy in the spectral region lying at longer wave lengths than 0.6 μ. Accordingly the furnace was set in position as for a run and a stream of cupric chloride solution was passed through the reaction vessel at a known rate, the temperature of the stream being taken at points on either side of the reaction vessel. Heating by conduction was reduced by passing a strong blast of air between the furnace and the window to such an extent that the average temperature of the air blast was maintained nearly the same as the temperature of the solution. Thus in one experiment the solution rose from 27.6 to 36.7° while the average temperature of the air blast was 38.2° and the time of flow for 500 cc. was 518 sec., giving a flux of 527 cal. per minute. The average of eight such experiments was 535 cal. per minute with a maximum deviation of 28 cal.

The effective black-body temperature of the furnace was then estimated by assuming some temperature and calculating from the geometry of the set-up and the transmission losses the corresponding flux in the reaction vessel. This was to be compared with the experimentally determined value and the assumed temperature corrected to give the correct flux. Thus the flux of radiation through a circular surface of diameter D from a circular black-body surface of the same diameter and parallel to the first at a distance d is given by[10]

$$F_\nu = \frac{1}{2D^2}\, c\, u_\nu T_\nu \left(\frac{D^2}{2} + d^2 - d\sqrt{D^2 + d^2}\right) \qquad (1)$$

---

[9] Coblentz, *Bulletin of the Bureau of Standards*, **9**, 110 (1913).

[10] J. W. T. Walsh, "Photometry," Constable and Co., London, 1926, p. 104.

where $F_\nu d\nu$ is the energy per unit area per second in the frequency range ν to $\nu + d\nu$, $u_\nu d\nu$ the density of radiant energy in the same frequency range, corresponding to the black-body temperature of the source, and c the velocity of light. T_ν is the fractional transmission of the intervening windows at the frequency ν.

The total flux was then obtained by graphical integration of Equation 1 over all values of ν using for u_ν the values given by the Planck radiation law, assuming a temperature of 800°, and for T_ν values obtained from Coblentz's[11] data on the transmission of mica.

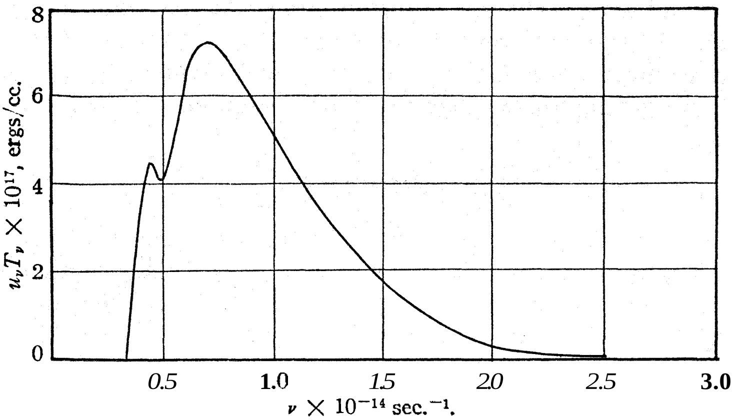


Fig. 2.—Transmitted energy distribution curve.

A plot of $u_\nu T_\nu$ against ν is shown in Fig. 2. The area under the curve was found to be 1.408×10^{-10} cal. per cc.

Substituting in Equation 1, $D = 5$ cm., $c = 3 \times 10^{10}$ cm./sec., $d = 2.2$ cm., one obtains

$$F_\nu d\nu = 3.19 \times 10^9 u_\nu T_\nu d\nu \text{ per sq. cm. per second} \tag{2}$$

$$F_{\text{total}} = \pi D^2/4 \times 3.19 \times 10^9 \times 60 \int_0^\infty u_\nu T_\nu d\nu = 529 \text{ cal. per min.} \tag{3}$$

Since the observed value was 535 cal. per min., it seems fair to treat the furnace as a black-body emitting at 800°, especially as the actual temperature over the greater part of the furnace was 40–50° above this, the temperature near the open end dropping to about 750°.

Intensity of Radiation.—In order to determine whether or not the radiation was of such an intensity that an observable change of rotation would have been noticed had the radiation been effective, we must compare the density of radiant energy which has been produced in the reacting substance with that in a hohlraum at the temperature of the liquid during the irradiation.

---

[11] Coblentz, "Investigations of Infra-red Spectra," *Carnegie Institution Publication Number* 65, 1907, Vol. III, p. 49.

The average intensity of radiation in the liquid layer as a fraction of the incident intensity can be obtained from the formula

$$\bar{I}/I_0 = \frac{1}{\alpha x_1}(1 - e^{-\alpha x_1})$$

where α is the absorption coefficient and x_1 the thickness of absorbing material.

Taking Coblentz's[11] data on pinene, the absorption coefficients α have been calculated at intervals over the range from 1 to 9μ, and, using these, values of $\bar{I}/I_0$ obtained from the above equation.

The flux of energy through the lower surface of the liquid is given by Equation 2. Making a correction for the slight divergence of the beam, multiplying by the average intensity ratio and dividing by the velocity of light, we get for the average radiation density of the frequency v the expression

$$\bar{u}_\nu = 2.57 \times 10^9 \frac{u_\nu T_\nu}{c} \frac{\bar{I}}{I_0}$$

Table II shows the values of 4, over the frequency range corresponding to wave lengths from 1 to 5.5μ, and also the values of the radiation density u_ν at 152" corresponding to the temperature of the liquid, the latter values being calculated from the Planck radiation law.

TABLE II

VALUES

$\lambda(\mu)$	$\nu \times 10^{-14}$	$\bar{u}_\nu \times 10^{19}$	$u_\nu \times 10^{19}$ (152°)
1	3	7.4×10^{-4}	3.69×10^{-9}
1.2	2.5	8.98×10^{-3}	3.84×10^{-7}
1.5	2	0.148	8.09×10^{-5}
2.0	1.5	0.805	9.85×10^{-3}
2.5	1.2	1.027	0.142
3	1	0.456	0.803
3.5	0.858	0.217	2.49
4	0.75	0.833	5.48
5	0.6	1.19	15.5
5.5	0.546	0.733	21.6

Figure 3 shows a plot of $\bar{u}_\nu$ and $u_\nu(t = 152°)$ against frequency v. It is to be noticed that out to a wave length of nearly 3μ the density of radiation produced is very much greater than that at 152°, so that if these shorter wave lengths were active the reaction rate should have been increased many times. The range of greatly increased intensity includes the red end of the visible and it is here we would expect an effect on the basis of the simple radiation hypothesis, since for pinene the total energy of activation corresponds to a wave length of 0.65μ. Past 3μ the induced density falls considerably below the other, so that these experiments do not furnish any information as to the effect of these longer wave lengths.

Discussion

The results obtained here show that radiation in the infra-red out to a wave length of 3μ does not accelerate the rate of racemization of pinene, and, therefore, that in this thermal reaction radiation over this range is not the agency which keeps up the quota of activated molecules. One must' still admit the possibility, however, of longer wave lengths being active, since at a temperature of 152° the maximum intensity of black-body radiation lies out as far as 12.5μ. Further, both N_2O_5 and pinene have strong absorption bands in the region beyond 3μ.[11,12]

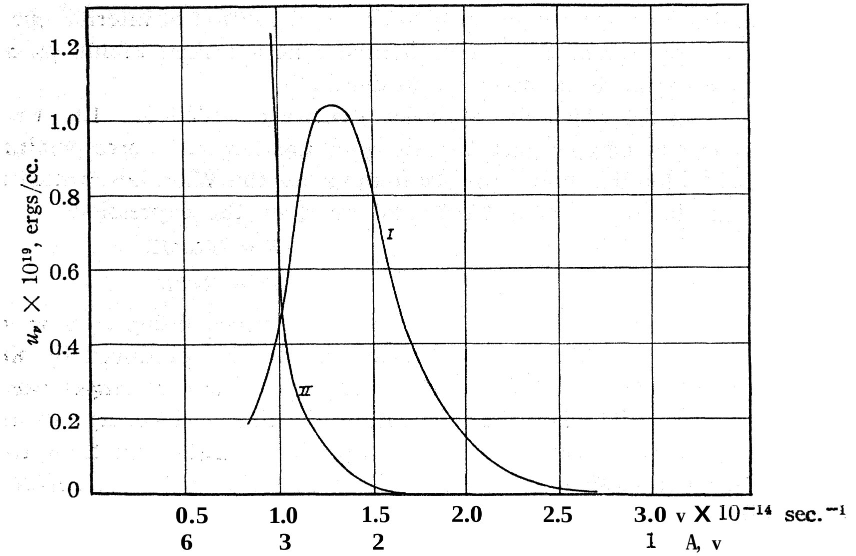


Fig. 3.—Energy distribution in liquid layer. I, Energy from furnace ($\bar{u}_\nu$). II, Black-body energy at 152".

Turning to the work of Lewis and Mayer, it appears at first sight as though they had extended the range of wave lengths over which radiation is shown to be inactive in this reaction out of 13μ. The method of treatment used by them, however, seems to require some further analysis. Under the conditions of their experiment, pinene coming from a nozzle at a temperature of 93° was shot through a radiation field corresponding to a black-body temperature of about 1000°K. and was condensed out on the farther side by liquid air. The length of time during which the molecules were exposed to the radiation was calculated to be 1.2×10^{-4} sec. To treat these data by the method which has been applied to the experiment just described, one may first ask the following question. By what factor is it necessary to increase the thermal reaction rate at 93° in order that it

---

[12] Daniels, THIS JOURNAL, 47, 2856 (1925).

may be observable during the time of exposure? Mayer has calculated that the minimum rate which he could have observed is $k_1 = 431$ sec.$^{-1}$, which would be the thermal rate at 800°K. By using the value here given of the reaction rate at 156° and extrapolating in the usual manner, one finds the thermal rate at 93° to be 4.68×10^{-12} sec.$^{-1}$. Hence the rate at 93° must be increased by a factor of 10^{14} if it is to be observable. This can take place in two ways, assuming that radiation is to be the activating agency. First, the density of radiation over the frequencies to be tested may be increased by a factor of 10^{14} over the corresponding densities in a hohlraum at 93°. Second, the molecules by successive absorption of quanta may be brought up to such a distribution of internal energies as would prevail at 800°, the thermal reaction then taking place. Let us now examine these processes in detail.

The frequency at which the radiation density at 1053°K., the temperature of the furnace, is just 10^{14} times as great as the corresponding density at 93° (366°K.) may easily be found from the Wien law, which is applicable in the region considered, and gives us the expression

$$\frac{u_\nu}{u_\nu'} = \frac{e^{h\nu/kT'}}{e^{h\nu/kT}} \quad \text{where} \quad \frac{u_\nu}{u_\nu'} = 10^{14} \quad \text{and} \quad \begin{array}{l} T = 1053\text{°K.} \\ T' = 366\text{°K.} \end{array}$$

This gives for ν the value 3.79×10^{14} sec.$^{-1}$, corresponding to a wave length of 0.79μ. At shorter wave lengths the density produced by the furnace is greater than 10^{14} times the density at 93° and at longer wave lengths it is less. (The fact that the actual distribution of energy in the furnace as used by Mayer was such as to produce densities at these frequencies two or three times that of black-body radiation at 1053°K. makes only a very slight change in this result.) Therefore, if we regard the molecules as remaining throughout the length of furnace substantially in the states which they have at 93°, then radiation has been proved to be inactive in this experiment only for wave lengths shorter than 0.79μ.

Now let us consider the second possibility that by successive absorption of quanta the molecules are distributed in states corresponding to a considerably higher temperature than 93° throughout a considerable portion of the length of the furnace. For the number of quantum jumps per second from a lower state i to a higher state j, we have the quantity $B_{ij}u_{\nu ij}$ where B_{ij} is Einstein's coefficient of absorption and $u_{\nu ij}$ is the radiation density at the frequency necessary to transfer the molecule from state i to state j. From correspondence principle considerations[13] a maximum value of B_{ij} can be given as of the order of 10^{20} c. g. s. units;[14] and taking

---

[13] See Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co., New York, 1927, p. 179.

[14] Undoubtedly some arbitrariness is introduced by the use of the value 10^{20} for B_{ij}. This has been set as a probable upper limit and actually from absorption data values of 10^{14} to 10^{19} have been obtained. Tolman, *Phys. Rev.*, 23, 693 (1924).

the maximum intensity in the black-body spectrum at 1073°K.[15] we should have $u_{\nu ij} = 9.75 \times 10^{-17}$ ergs-sec. per cc., giving us about 10^4 jumps per second as the maximum possible number that could take place for any given absorption line. Thus in the 1.2×10^{-4} seconds taken to pass through the furnace a molecule could not make more than one jump on the average for each absorption line that it had in the neighborhood of the maximum intensity of radiation; while the number of jumps for lines of other frequencies would be even less. If this be so, the distribution of molecules among the energy states throughout the whole length of Mayer's tube may not have been appreciably different from that prevailing at 93°.

Hence Mayer's experiment has not proved the ineffectiveness of radiation out to 13μ in the *thermal* racemization of pinene, hut has shown that in the short length of time during which the molecules remained in his furnace, radiation corresponding approximately to 1053°K. was not able to raise his molecules from states corresponding to 93° to states high enough so that the reaction was appreciable.

The foregoing discussion makes evident the desirability, in testing the radiation hypothesis, of working in the presence of excess radiation *at temperatures* where the thermal rate is already appreciable,[16] as was done in the present experiments.

Summary

1. Experiments are described which show that the rate of racemization of pinene is not accelerated by a large increase in the density of radiation over the range of wave lengths out to 3μ.

2. The nature of the experiments does not warrant any conclusion as to the effectiveness of wave lengths longer than 3μ.

3. The work of Lewis and Mayer on pinene is criticized from the point of view of the justifiability of the conclusions which they drew as to the inactivity of the longer wave lengths, and it is shown that they have not proved that radiation of wave lengths out as far as 13μ is inactive in the thermal racemization of pinene.

PASADENA, CALIFORNIA

---

[15] The temperature used here is slightly higher than that given by Mayer. It is, however, more favorable to a high rate of activation and was used since data at this temperature were available.

[16] Compare Tolman, THIS JOURNAL, 47,1549 (1925), and ref. 13, p. 283.

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

ACTIVITY COEFFICIENT OF DIACETONE ALCOHOL IN AQUEOUS SALT SOLUTIONS

BY GÖSTA ÅKERLÖF

RECEIVED AUGUST 7, 1928 PUBLISHED APRIL 5, 1929

Introduction

Our present theories for the velocity of catalyzed reactions in concentrated solutions of strong electrolytes are handicapped because little is known concerning a number of the variables which may have to be considered. For an ever-increasing number of reactions we know quite definitely that the velocity is either a function of or parallel to the thermodynamic activities of the electrolytes present. Thus far our knowledge of the influence of changes of the activity coefficients of the reacting substance is very incomplete. This investigation has been carried out in order to get an idea of the magnitude of the changes of the relative activity coefficient of diacetone alcohol in concentrated hydroxide–salt solutions. Experimental methods suitable for this study were limited both in number and accuracy. The changes in partition coefficient between the salt solutions and an insoluble organic liquid have been utilized.

Experimental Method

According to Gibbs the activity of a certain component is the same in all phases of a polyphase system in equilibrium at constant temperature. The activity is defined as the product of the activity coefficient γ and the concentration c

$$\gamma_1 c_1 = \gamma_2 c_2 = \gamma_3 c_3 = \ldots$$

where the subscripts denote the different phases. Let us assume that the activity coefficient of diacetone alcohol in pure water has the value of unity. Dissolved in another solvent, as toluene, the activity coefficient may be considered as a constant and independent of the concentration, because the partition coefficient with pure water is a constant. We then obtain for the activity coefficient of diacetone alcohol in a salt solution

$$\gamma = k \times c_1/c_2$$

where k is the partition coefficient with pure water and c_1 and c_2 are the concentrations of the diacetone alcohol in the salt solution and toluene, respectively. These values are measured simultaneously.

To determine these concentration changes a Zeiss interferometer was employed. After some difficulties in obtaining clear spectra for solutions with solvents other than water had been overcome, the following procedure was adopted. First a series of salt solutions was made up in 500-cc. Erlenmeyer flasks. All salt concentrations were calculated as weight normality. The amount of water used was 400 g. at lower concentrations and 300 g. at higher ones. Usually a very carefully filtered, highly concentrated standard solution of the salt was used for making up the solutions. Most of the C. P. or analyzed chemicals used contained a large amount of dust.

After the salt solution had been given a careful mixing, about 50 cc. was poured over the edge of the flask, which was slowly rotated. Immediately after this, amounts of solution containing 100 g. of water were weighed off in two 250-cc. Erlenmeyer flasks with ground-glass stoppers. In order to avoid evaporation of water the weighing had to be done rapidly. The average accuracy of the weighing was about 0.1--0.2 g. Wetting of the ground surface inside the neck of the flasks by the solutions was avoided. To one of these weighed solutions was added 100 cc. of solvent containing about 1% of diacetone alcohol and to the other one also 100 cc. of solvent but with only 0.2% of the alcohol present. It was found that when the pure solvents used were shaken with an aqueous salt solution rather stable emulsions were formed. The addition of a small amount of diacetone alcohol seemed to prevent this and the solutions cleared rapidly. The difference in diacetone alcohol concentration of the two different samples of the solvent added to the salt solutions was measured very carefully.

After the solvent had been added the glass stoppers to the flasks were wetted with two or three drops of the solvent, rotated with a slight pressure until an optically clear joint had been obtained and finally pressed in hard. Then the flasks were shaken vigorously three or four times for three to five-minute periods at intervals of about one hour. Tests of the efficiency of the shaking seemed to show that after the second one the differences obtained probably were caused by other experimental errors. After the last shaking had been completed the solutions were left for twenty-four hours so that they became perfectly clear. If the measurements were started shortly after the last shaking the results seemed to be very erratic. The enormous sensitivity of the interferometer and the very small concentration differences that had to be used, required optically clear solutions.

For the measurement the two layers in each flask were first separated. The upper one was removed by pouring the greater part of the liquid slowly over the edge of the flask into a 150-cc. Erlenmeyer flask, which was immediately closed with a rubber stopper. A small separatory funnel was used to obtain the lower layer free from the upper one. The remaining solution was poured slowly into the funnel and then withdrawn ten to fifteen minutes later. It was found to be desirable to obtain the amount of diacetone alcohol in the salt solution indirectly. The solutions containing salt were therefore thrown away and only the solvent solutions were used for the measurement.

The difference between the apparent total amount of diacetone alcohol present and that retained by the organic solvent after shaking with the salt solution, gave the amount in the latter. This gives the following equation for the calculation of the activity coefficient of the diacetone alcohol

$$\gamma = \frac{R_0 - R_1}{R_1} \times \frac{R_2}{R_0 - R_2}\ .$$

where R_0 is the reading for the original solvent solutions, R_1 after shaking with water and R_2 after shaking with the salt solution (all values corrected).

The solutions were now ready to be used. The two compartments of the all-glass cells belonging to the interferometer were washed out carefully three or four times with their respective solutions, then filled to overflowing and the glass covers put on in such a way that no air bubbles were inclosed. Finally the cell was wiped dry, the end-plates polished and the cell placed in the little kerosene bath of the interferometer. Water could not be used for the bath, because it was impossible to remove all of the solvent from the outside of the cell by wiping, due to the afterflow from the casing around the upper part of the cell. When placed in water the thin oil film on the surface of the end-plates became uneven, which completely distorted or entirely blotted out the spectra. The correct reading of the interferometer was very difficult. The distance between two spectral bands was about 16 units on the scale. The greatest difficulty was to choose the right bands. At times four or five bands in the upper spectrum appeared to have nearly the same color and by pairs to coincide with the two middle bands of the lower spectrum. An error of three or four times 16 units, therefore, could easily be made. This necessitated high sensitivity to small variations in color and considerable experience in judging the appearance of the bands.

When the cells had been placed in the interferometer bath the liquid was stirred slowly at the rate of about twenty to forty turns a minute. The time required to get a reading varied between five and twenty minutes. Too rapid stirring caused splashing and usually gave very poor spectra. When the rate was too slow the time necessary to obtain a good reading lengthened considerably and sometimes also gave distorted spectra. Splashing of the bath liquid was rather difficult to avoid because the bath had to be kept nearly full and kerosene has a low viscosity. Exchange of kerosene for other liquids with higher viscosity (as ethyl phthalate) brought in other disadvantages which were considered as far from serious. Kerosene evaporating from the outside of the bath slowly attacked the Canada balsam with which the prisms of the interferometer were fastened. This caused continuous changes of the zero point of the instrument. In order to avoid these changes the commercial kerosene was fractionated and the fraction boiling around 350" was used. This decreased to a large extent the zero point changes. They amounted only to a few units a week.

A large number of solvents were tried out for these experiments. Solvents with low boiling point and high volatility, like toluene or benzene, could not be used. Bromobenzene and cymene were finally selected as most suitable. The former was first washed by inside spraying with water for four to five hours. The water velocity was about 2-3 liters a minute. At higher velocities emulsions were formed. Then the solvent was dried with fused calcium chloride and vacuum distilled in a large all-glass still. The commercial cymene was first distilled three times from concentrated potassium hydroxide solution. It was then washed in a continuous stream of water for four to five hours, dried and redistilled in high vacuum. When shaken with water this solvent separated rapidly and became perfectly clear. The diacetone alcohol was used as obtained from Eastman Kodak Co. It contained slight traces of water but attempts at further drying failed. Mesityl oxide and water were formed. The former is insoluble in the latter and therefore separated upon further addition of water. However, the amount of impurities present was too small to affect the results perceptibly.

Correction of the Interferometer Readings

The readings on the interferometer were not exactly proportional to the diacetone alcohol concentration. With increasing concentration the correction necessary to obtain proportionality with the true values increased. At the end of the scale the correction amounted to about 300 units. The correction curve seemed to be characteristic for the instrument and independent of the nature of the solvent employed. Table I gives a summary of the measurements for the determination of the correction curve.

For the calculation of the experimental results which will be presented below, the corrections were obtained graphically. The corrections necessary when the diacetone alcohol concentration in the salt solution phase also is measured directly might be indicated here. Diacetone alcohol has a higher refractive index than water. The addition of salt to pure water gives a higher refractive index to the solution. A given

TABLE I

MEASUREMENTS FOR CORRECTION CURVE OF THE INTERFEROMETER

I. WATER SOLUTIONS

W. D. A.[a]	Obs. value. A	Interp. value, B	Ratio 10^{-1} B/W. D. A.	Corr. value	Error of B
0.00	0000	0000	270	0000	000
.10	0273	0273	273	0270	003
.20	0549	0552	276	0540	012
.30	0837	0837	279	0810	027
.40	1122	1128	282	1080	048
.50	1427	1426	285	1350	075
.60	1722	1728	288	1620	108
.70	2034	2037	291	1890	147
.80	2342	2352	294	2160	192
.90	2677	2673	297	2430	243
1.00	3004	3000	300	2700	300
		II. CYMENE SOLUTIONS			
C. D. A.					
0.00	0000	0000	143[b]	0000	000
1.00	0143	0143	143	0143	000
2.00	0289	0288	144	0286	002
3.00	0437	0435	145	0429	006
4.00	0589	0584	146	0572	012
5.00	0741	0735	147	0715	020
6.00	0893	0888	148	0858	030
7.00	1051	1043	149	1001	042
8.00	1207	1200	150	1144	056
9.00	1369	1359	151	1287	072
10.00	1522	1520	152	1430	090
		III. BROMOBENZENE SOLUTIONS			
C. D. A.					
0.00	0000	0000	272	0000	000
1.00	0277	0275	275	0272	003
2.00	0561	0556	278	0544	012
3.00	0837	0843	281	0816	027
4.00	1126	1136	284	1088	048
5.00	1428	1435	287	1360	075
6.00	1719	1740	290	1632	108
7.00	2034	2051	293	1904	147
8.00	2370	2368	296	2176	192
9.00	2692	2691	299	2448	243
10.00	3017	3020	302	2720	300

[a] W. D. A. gives the amount of diacetone alcohol present in weight per cent. For cymene and bromobenzene, standard solutions containing 6.978 volume per cent. of diacetone alcohol were used. C. D. A. gives the number of cc. of these solutions diluted to a total of 100 cc.

[b] This value instead of 142 was used because it gave better agreement with the measurements for water and bromobenzene solutions.

amount of diacetone alcohol must then cause a smaller deviation in the interferometer when dissolved in the salt solution as compared with the one for pure water. With the proper scale correction applied, a linear decrease is obtained with increasing salt concentration. After correcting for scale deviation, the reading obtained for the salt solution used in the partition experiment and multiplying with the corrected decrease ratio for the salt solution used, all measurements are comparable and give the correct activity coefficient. However, this method is quite complicated to carry out and should ordinarily be avoided.

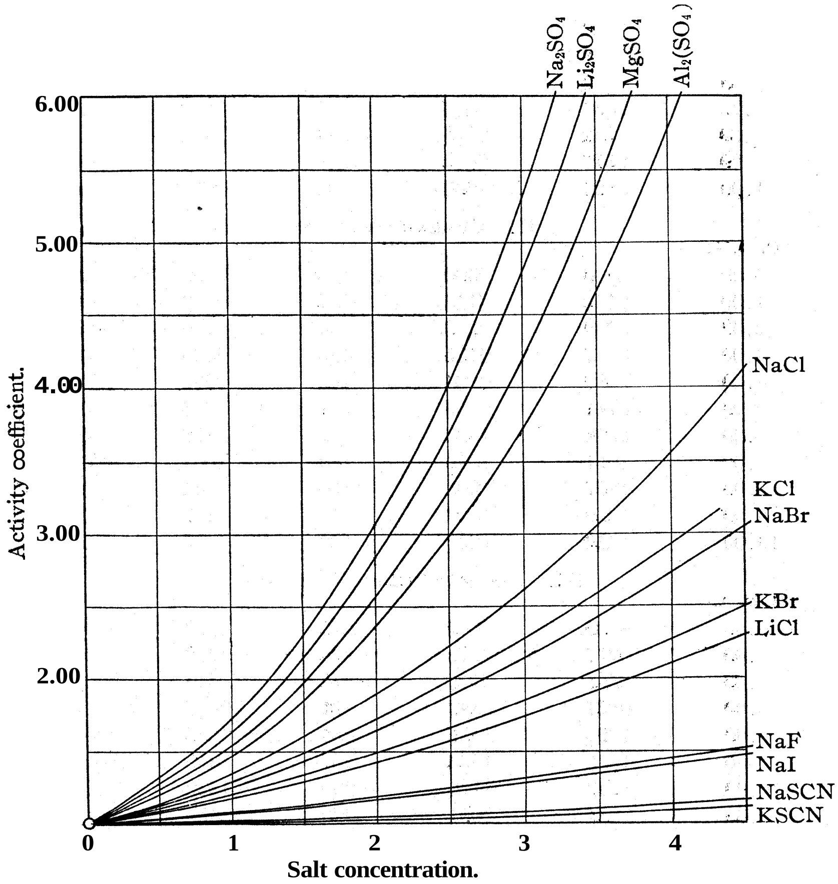


Fig. 1.—Curves for the relative activity coefficient of diacetone alcohol in various salt solutions.

Experimental Results

Table II gives a summary of the measurements. All interferometer readings are the uncorrected values. The temperature for the measurements was on the average 24° with a maximum variation of about one degree. A suitable thermostat was not available but the temperature coefficients seem to be quite small or negligible. The general accuracy of the results is a little difficult to judge but most probably the relative errors in the distribution of the curves seldom exceed 5%. The results are also independent of the nature of the solvents used, that is, the same values were obtained either for bromohenzene or cymene (a mixture of ethyl phthalate and bromobenzene also gave the same result). Up to the limit of the concentration that could be used for diacetone alcohol, the activity coefficients obtained seemed to be independent of the concentration either in the organic solvent phase or the salt solution used. All salt concentrations in Table II are expressed in weight normality per 1000 g. of water. Fig. 1 gives the curves for the measurements at increasing salt concentrations; Fig. 2 is the curve for the logarithm of the activity coefficients at constant total molarity in sodium–lithium chloride solutions. Fig. 3 shows the corresponding curves at varying constant total molarity. All curves in this last figure are drawn as straight, parallel lines because this seemed best to represent the results. It gives an analogy to the curves obtained by Åkerlöf[1] for the decomposition velocity of diacetone alcohol in alkali hydroxide–salt solutions at varying constant total molarity.

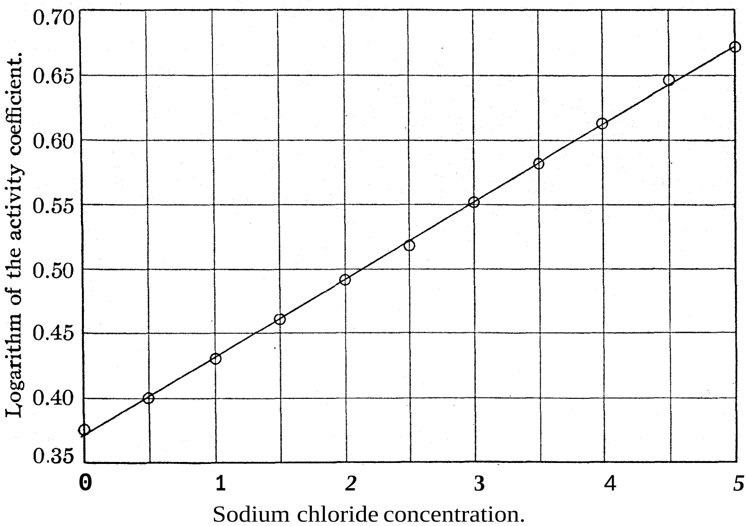


Fig. 2.—Curve for the logarithm of the relative activity coefficient of diacetone alcohol in sodium–lithium chloride solutions at constant total normality of 5 N.

Table II also contains the values for (log γ)/N. These values seem

---

[1] Åkerlöf, This Journal, 49, 2955 (1927).

to be fairly constant. Randall and Failey[2] have recently shown that this probably is true for non-electrolytes in salt solutions. In Table III is given a comparison between the values for the activity coefficients of a few gases in 2 N sodium and potassium chloride and sodium sulfate solutions and those obtained for diacetone alcohol in the same salt solutions,

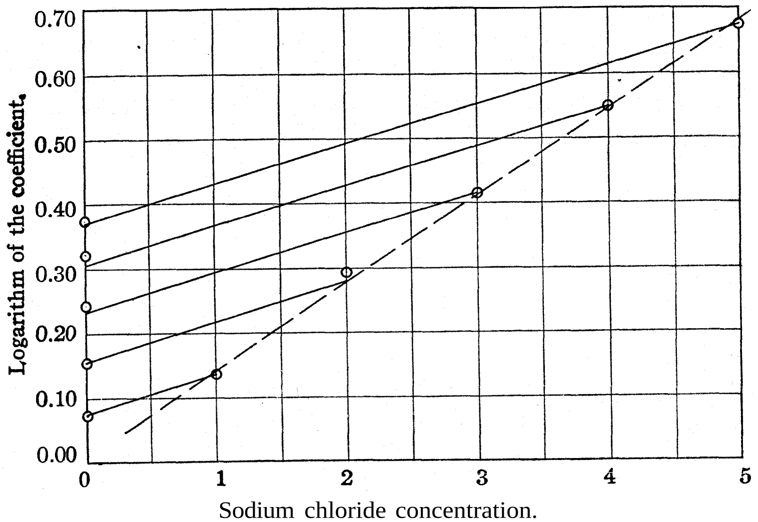


Fig. 3.—Curves for the logarithm of the relative activity coefficient of diacetone alcohol in sodium–lithium chloride solutions at varying constant total normality.

Considering the large probable errors of the solubility measurements used for the calculation of the activity coefficients of the gases, we might perhaps be justified in assuming them to be approximately independent of the nature of the gas employed or constant for a given salt solution.

TABLE II

RELATIVE ACTIVITY COEFFICIENT OF DIACETONE ALCOHOL IN SALT SOLUTIONS

N	R	r	(log γ)/N	R	r	(log γ)/N	R	r	(log γ)/N
	NaCl Solutions			KCl Solutions			NaBr Solutions		
0.00	326	1.00	...	326	1.00	...	628	1.00	...
1.00	432	1.37	0.136	416	1.31	0.118	756	1.28	0.107
1.50	507	1.66	.146	465	1.50	.118	...	...	...
2.00	582	1.97	.147	520	1.72	.117	920	1.68	.113
2.50	650	2.27	.141	593	2.02	.122	...	...	...
3.00	724	2.62	.139	648	2.26	.118	1057	2.09	.107
3.50	810	3.05	.138	706	2.53	.115	1180	2.50	.111
4.00	900	3.55	.137	793	2.97	.118	1248	2.76	.110
4.50	987	4.07	.135	...	...	...	1319	3.05	.108
5.00	1083	4.71	.135	...	...	...	1393	3.39	.106
	Mean		.139	Mean		.118	Mean		.109

---

[2] Randall and Failey, Chemical *Reviews*, 4,271,285,291 (1927).

TABLE II *(Continued)*

N	*R*	γ	(log γ)/*N*	R	γ	(log γ)/*N*	*R*	γ	(log γ)/*N*
	KBr Solutions			NaI Solutions			KI Solutions		
0.00	628	1.00	...	628	1.00	...	628	1.00	...
1.00	735	1.23	0.0902	680	1.10	0.0449	665	1.08	0.0320
1.50	...	...	...	705	1.16	.0440	682	1.11	.0310
2.00	860	1.53	.0923	725	1.21	.0410	707	1.17	.0336
2.50	...	...	...	749	1.26	.0404	736	1.23	.0363
3.00	977	1.84	.0882	776	1.33	.0409	759	1.29	.0365
3.50	1043	2.04	.0887	795	1.37	.0394	775	1.32	.0347
4.00	1116	2.29	.0898	822	1.43	.0391	802	1.39	.0391
4.50	1177	2.49	.0900	...	...	....	...	...	...
5.00	1258	2.82	.0900	...	...	....	...	...	...
		Mean	.0900		Mean	.0414		Mean	.0342
	LiCl Solutions			NaSCN Solutions			KSCN Solutions		
0.00	628	1.00	...	628	1.00	...	628	1.00	...
1.00	715	1.18	0.0732	641	1.03	0.0115	636	1.02	0.0071
1.60	...	...	...	...	...	...	...	...	...
2.00	818	1.43	.0766	655	1.06	.0117	652	1.05	.0104
2.50	...	...	...	....			...	...	...
3.00	942	1.75	.0807	664	1.08	.0106	659	1.06	.0090
3.50	985	1.87	.0776	671	1.09	.0107	665	1.08	.0092
4.00	1062	2.10	.0806	680	1.10	.0112	673	1.09	.0098
4.50	1112	2.27	.0790	686	1.12	.0111	680	1.10	.0100
5.00	1141	2.37	.0765	691	1.13	.0108	685	1.12	.0098
		Mean	.0774		Mean	.0111		Mean	.0093
	Na_2SO_4 Solutions			Li_2SO_4 Solutions			$MgSO_4$ Solutions		
0.00	326	1.00	...	326	1.00	...	326	1.00	...
1.00	520	1.71	0.233	514	1.69	0.227	488	1.59	0.200
1.50	639	2.22	.230	....			...	...	...
2.00	812	3.06	.242	768	2.84	.226	698	2.49	.198
2.50	976	4.00	.241	...	...	...	...	...	...
3.00	1167	5.33	.242	1069	5.04	.234	1004	4.18	.207
3.50	...	...	...	1337	6.81	.238	1172	5.37	.208
4.00	...	...	...	1496	8.33	.230	1390	7.33	.216
4.50	...	...	...	1548	9.17	.214	1537	10.4	.226
6.00	...	...	...	1823	13.5	(.265)	1755	12.4	.218
		Mean	.238		Mean	.228		Mean	.210
	$MgCl_2$ Solutions			$AlCl_3$ Solutions			$Al_2(SO_4)_3$ Solutions		
0.00	312	1.00	...	312	1.00	...	312	1.00	...
1.00	379	1.24	0.094	368	1.20	0.080	454	1.54	0.188
2.00	457	1.55	.095	445	1.50	.088	633	2.34	.184
3.00	547	1.95	.099	523	1.83	.087	882	3.70	.189
4.00	633	2.33	.092	628	2.31	.091	1186	5.99	.194
5.00	726	2.82	.090	707	2.71	.087	1492	9.52	.195

N is the salt concentration in weight normality. R is the interferometer reading for the bromobenzene or cymene phase. Pure water and bromobenzene gave R = 628 with a diacetone alcohol total of R = 2825, both in the bromobenzene phase. Pure water and cymene gave (1) R = 326 for a diacetone alcohol total of R = 2824 and (2) R = 312 for an alcohol total of R = 2682, all values for the cymene phase.

TABLE II (*Concluded*)

MEASUREMENTS WITH NACL–LICL SOLUTIONS AT CONSTANT TOTAL NORMALITY OF 5 N

Bromobenzene used as solvent for these measurements

NaCl	LiCl	R	γ	log γ
0.00	5.00	1141	2.37	0.375
0.50	4.50	1182	2.51	.400
1.00	4.00	1230	2.69	.430
1.50	3.50	1280	2.89	.461
2.00	3.00	1330	3.10	.492
2.50	2.50	1375	3.30	.519
3.00	2.00	1430	3.57	.552
3.50	1.50	1478	3.82	.582
4.00	1.00	1530	4.12	.614
4.50	0.50	1583	4.44	.647
5.00	.00	1622	4.70	.672

TABLE III

ACTIVITY COEFFICIENTS FOR GASES IN 2 N NACL, KCL AND NA_2SO_4 SOLUTIONS

	NaCl	KCl	Na_2SO_4
Oxygen	1.83	1.70*	1.93[a]
Hydrogen	1.55	1.45	...
Nitrous oxide	1.59	1.45	2.14
Acetylene	1.54	1.35	2.00
Hydrogen sulfide	1.32	1.28	3.47
Mean	1.56	1.45	2.39
Diacetone alcohol	1.90	1.72	3.00

[a] Values obtained from data in Abegg-Auerbach, "Handbuch der anorg. Chemie," **6**, 1 (1927). Other data from Randall and Failey.

If this is the case we apparently obtain the same or at least a very similar distribution of the curves for the activity coefficients of the gases in salt solutions as for those of diacetone alcohol.

Discussion of the Results

These measurements were undertaken in order to determine, if possible, whether or not the decomposition velocity of diacetone alcohol in alkali-hydroxide–salt solutions was influenced by changes in the activity coefficient of the reacting substance. In Fig. 4 are given some of the curves for the relative activity coefficients of ethyl acetate in various salt solutions as calculated from the solubility measurements of Glasstone and Pound.[3] A comparison of these curves with those in Fig. 1 shows a very striking similarity. Their distribution is nearly the same in both cases. In Fig. 5 are the curves for the velocity of hydrolysis of ethyl acetate by 0.1 N hydrochloric acid in various salt solutions.[4] Fig. 6 shows the corre-

---

[3] Glasstone and Pound, *J. Chem. Soc.*, 127, 2660 (1925); *cf.* further Glasstone, Dimond and Jones, *ibid.*, 128, 2935 (1926).

[4] Data for Fig. 5 obtained from Harned, THIS JOURNAL, 40, 1461 (1918); Bowe, *J. Phys. Chem.*, 31, 290 (1927)

sponding curves for the decomposition of diacetone alcohol in 0.1 *N* alkali hydroxide-salt solutions.[5] In the case of ethyl acetate there is a great similarity between the distribution of the curves for velocity and activity coefficients. For diacetone alcohol the two sets of curves are also distributed in a similar manner, although their direction is widely different. For sodium chloride solutions the velocity decreases and activity coefficient increases rapidly. The curves for sodium sulfate, chloride, bromide, iodide and sulfocyanide solutions follow each other in the same order and at about the same distance in relation to each other. The position of the activity curves for potassium salt solutions below those for sodium salts are exceptions to identical distribution of activity and velocity curves.

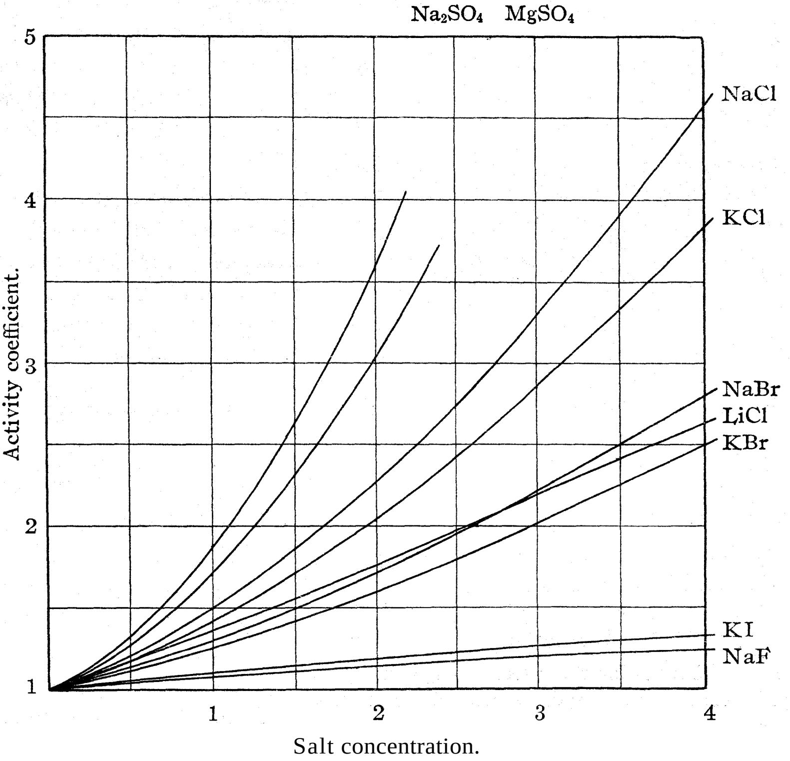


Fig. 4.—Curves for the relative activity coefficient of ethyl acetate in various salt solutions as calculated from solubility measurements of Glasstone and Pound, and Glasstone, Dimond and Jones.

In view of these facts we might feel inclined to believe that in the case of ethyl acetate velocity and activity of the reacting substance are

---

[5] Data for Fig. 6 are obtained from Åkerlöf, This Journal, 48,3046 (1926).

intimately connected. The data at present available are not very accurate but it seems as if this could be the case.[6] The use of a similar explanation for diacetone alcohol appears to offer great difficulties because direction and distribution of velocity and activity curves are not always the same. Decrease in velocity and increase of activity would give the velocity as an inverse function of the activity, while for sulfate solutions where both velocity and activity increase with increasing salt concentration, the former apparently would be proportional to a function of the latter.

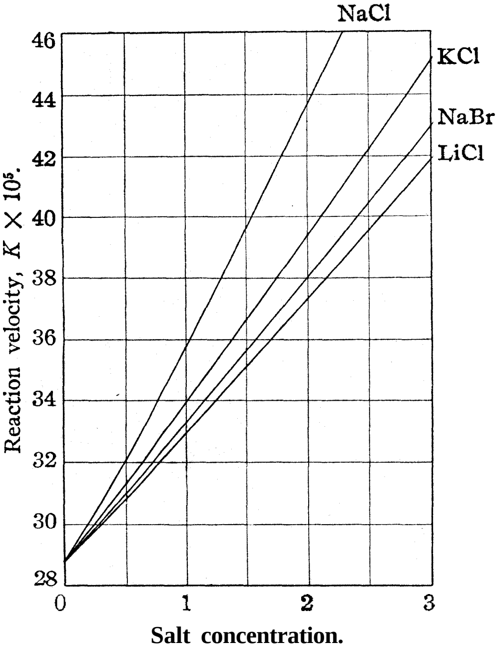


Fig. 5.—Curves for the velocity of hydrolysis of ethyl acetate by 0.1 N hydrochloric acid in various salt solutions.

According to the theory of Brönsted,[7] the velocity of a simple chemical reaction, which does not give definite intermediary products, is given by the equation

$$v = k(\mathrm{A})(\mathrm{B}) \frac{\gamma_{\mathrm{A}} \times \gamma_{\mathrm{B}}}{\gamma_{\mathrm{X}}}$$

where v is the velocity, k is a constant, (A) and (B) are the concentration of the two reacting substances A and B and γ_{A}, γ_{B} and γ_{X} are activity coefficients of A, B and X. The latter is a collision compound of momentary existence. If A is an ion, the intermediate is also an ion with the same valence. Then the velocity is proportional to the concentration of the reacting ion and the activity coefficient of the substance B.

Previously it has been shown by Åkerlöf[8] that the decomposition velocity of diacetone alcohol in pure aqueous solutions of the alkali hydroxides at higher concentrations is proportional to the activity coefficients of the hydroxides. Furthermore, the consideration of the velocity as a function of the activity of the reacting substance leads to different equations for different salts present. Adhering to the validity of the equation

---

[6] Harned and Åkerlöf, *Trans. Faraday Soc.*, 24, 666 (1918).

[7] Bronsted, *Z. physik. Chem.*, 102, 169 (1922); *ibid.*, 115, 337 (192.5); *cf.* further Bjerrum, *ibid.*, 108, 82 (1924); *ibid.*, 118, 251 (1925); Christiansen, *ibid.*, 113, 35 (1924).

[8] Åkerlöf, THIS JOURNAL, 49, 2966 (1927).

of Bronsted, this may indicate that the activity coefficient of diacetone alcohol is canceled by γ_X. Then we must also assume that X is formed by the addition of both cation and anion of the hydroxide and has the character of a neutral molecule. This would give the velocity as being proportional to the concentration of the hydroxide and as a function of the activity coefficient of the same in qualitative agreement with the measurements.

If this explanation approaches the true conditions, we could expect to find the same or at least a very similar distribution of the curves for velocity and activity coefficients of the hydroxides in hydroxide–salt solutions. When the salt present decreases the velocity this conclusion seems to be approximately valid, as shown in Fig. 7.[9] The sulfate solutions might seem to be an exception and therefore make our explanation questionable. On the other hand, the sulfates increase the activity coefficients of the reacting substance very rapidly and this increase is relatively many times larger than the increase in reaction velocity at corresponding salt

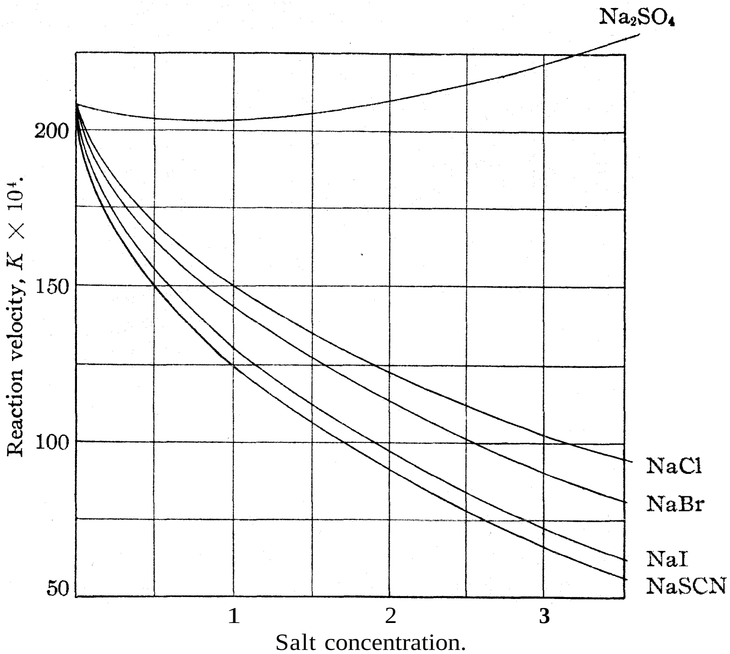


Fig. 6.—Curves for the decomposition velocity of diacetone alcohol in 0.1 N alkali hydroxide–salt solutions.

---

[9] Data for Fig. 7 are from measurements of Åkerlöf, THIS JOURNAL, 48, 3046 (1926); ibid., 48, 1160 (1926); Harned, *ibid.*, 47, 684, 689 (1925); Harned and James, *J. Phys.* Chem., 30, 1060 (1926); Douglas, "Tbesis," University of Pennsylvania, 1926.

concentrations. Most probably this must tend to cause larger deviations from a function of the activity of the electrolytes present.

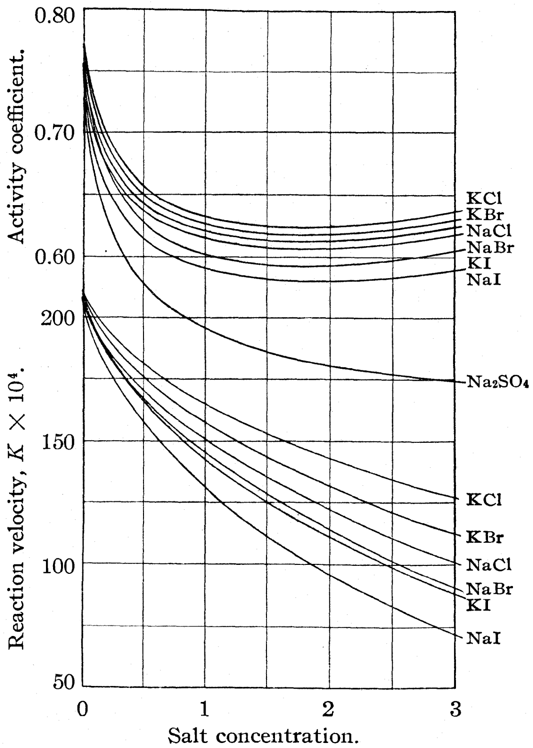


Fig. 7.—Curves for the decomposition velocity of diacetone alcohol in 0.1 *N* alkali hydroxide–salt solutions and the curves for the activity coefficient of the hydroxides in the same salt solutions.

Summary

The relative activity coefficient of diacetone alcohol in various salt solutions at 24 ± 1° has been measured, using an interferometric method to determine the partition coefficient of diacetone alcohol between the salt solutions and an insoluble organic liquid.

The results obtained agree closely in order of magnitude and distribution with the results of the calculation of the activity coefficient of ethyl acetate in the same salt solutions from solubility measurements of Glasstone and Pound. The relative activity coefficients for some permanent gases in these salt solutions are apparently also of the same order of magnitude and give most probably the same distribution as obtained for diacetone alcohol and ethyl acetate.

A short discussion has been given of the relation of these results to the theory of Bronsted of velocity of reactions catalyzed by strong electrolytes. It seems to be very difficult to find a thoroughly satisfactory explanation of the changes of the decomposition velocity of diacetone alcohol in various solutions of strong electrolytes.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY, UNIVERSITY OF LIVERPOOL]

THE SOLUBILITIES OF LEAD PHOSPHATES[1]

BY HORACE MILLET AND MAURICE JOWETT

RECEIVED AUGUST 20, 1928 PUBLISHED APRIL 5, 1929

Although some measurements have been made of the solubilities of the secondary and tertiary phosphates of lead in water, no measurements have been made under conditions sufficiently well defined to allow of calculation of the solubility products of these salts, and hence to allow of calculation of the solubilities under various conditions.

The solubilities of these salts are of biological interest in connection with lead poisoning and the lead treatment of cancer. Some evidence has been obtained by Aub and others,[2] and by Brooks[3] that inorganic lead compounds are transformed into lead phosphate in the body, lead phosphate being regarded as the least soluble salt of lead under body conditions.

The solubility of lead phosphates is thus probably the limiting factor with regard to lead-ion concentrations in the body, and the subject has been discussed from this point of view by W. C. M. Lewis.[4] The work of Fairhall[5] shows that the primary phosphate of lead, $PbH_4(PO_4)_2$, is much more soluble than the other phosphates except in very acid solutions and this salt is thus of no great biological importance.

We are not concerned here primarily with the biological aspects of the subject, the purpose of the present paper being to present measurements undertaken to determine the solubility products of the secondary and tertiary phosphates of lead. We shall, however, show reason to correct the statement[2] that whereas the tertiary phosphate is the stable salt under normal body conditions, a slight shift of equilibrium to the acid side converts this salt to the secondary phosphate.

---

[1] This investigation was undertaken on behalf of the Liverpool Medical Research Organization, Professor W. Blair Bell, Director, University of Liverpool.

[2] Aub, Fairhall, Minot and Reznikoff, "Monograph on Lead Poisoning," Williams and Wilkens Co., Baltimore, 1926.

[3] Brooks, *Biochem. J.*, **21**, 766 (1927).

[4] W. C. M. Lewis, *J. Cancer Research*, 11, 16 (1927).

[5] Fairhall, THIS JOURNAL, 46, 1593 (1924).

Methods

Measurements of hydrogen-ion activity were carried out with the quinhydrone electrode, as described in an accompanying paper.[6]

Phosphates were estimated by the colorimetric method of Briggs,[7] which is accurate to 1–2% under the conditions maintained.

The lead-ion activity in the lead phosphate solutions has been determined by employing a lead electrode in a cell of the following type

Pb | Solution of lead salt ¦ Saturated KCl | Normal calomel electrode

Getman[8] has shown that lead can function as a reversible electrode, a finding which has been confirmed by us.

The value of E_0 for the lead electrode at 25° has been taken to be 0.122 volt;[9] hence the value of $p\mathrm{Pb}^{++}$, the negative logarithm of the lead-ion activity, is obtained from the relation

$$p\mathrm{Pb}^{++} = \frac{E - 0.4042}{0.02956}$$

where E is the observed e.m.f. of a cell of the type shown above.

The corresponding formula for 37.5' has been taken to be

$$p\mathrm{Pb}^{++} = \frac{E - 0.4106}{0.03080}$$

As no value of E_0 for the lead electrode was available **for** 37.5°, **this** was determined by measurements on several dilute solutions of lead nitrate at both 25 and 37.5°, the activity coefficient of lead-ion being assumed to be the same in both cases.

The lead electrodes were made by depositing lead electrolytically upon platinum, using very weak currents. (For use in acid solutions, the electrodes were amalgamated.) The technique of the lead electrode will be described more fully elsewhere by one of the authors.

Tertiary lead phosphate was made, following Alders and Stähler,[10] by adding slowly in dilute solution an equivalent amount of Na_2HPO_4 to a dilute boiling solution of lead acetate, the precipitate being washed repeatedly.

Secondary lead phosphate was prepared by adding in the hot 16.5 *g.* of lead nitrate dissolved in 500 cc. of water to 8 g. of potassium dihydrogen phosphate dissolved in 500 cc. of *N*/6 nitric acid. The precipitate was kept in the mother liquor at 25° for two days and then washed and dried.

The solutions for solubility determinations, to which a considerable excess of the appropriate solid salt was added, were kept in a thermostat

[6] Jowett and Millet, THIS JOURNAL, **51,** 1004 (1929).

[7] Briggs, *J. Biol. Chem.*, 59, 255 (1924).

[8] Getman, THIS JOURNAL, **38,** 792 (1916); 40, 611 (1918).

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

[10] Alders and Stähler, *Ber.*, 42, 2261 (1909).

at the required temperature for several weeks before measurements were made, and evidence was obtained with each series that the lead-ion activities had reached practically constant values. Measurements of P_H were made on each solution on the same day that the lead-ion activity was measured and samples were simultaneously filtered for determination of phosphate.

General Considerations

In earlier measurements on the solubilities of the phosphates of lead[2] the importance of hydrogen-ion activity in determining the state of ionization of the phosphate was little considered. Since the solubility products of the phosphates are defined by the relations

$$S_2 = a_{\text{Pb}^{++}} \times a_{\text{HPO}_4^{--}} \qquad (1)$$
$$S_3 = a^3_{\text{Pb}^{++}} \times a^2_{\text{PO}_4^{---}} \qquad (2)$$

it is necessary to determine accurately the distribution of the total phosphate in solution between the various phosphate ions.

With this purpose in view the authors have determined values for the ionization constants of phosphoric acid.[3] The values required for our purposes are given in Table I. They are defined as follows

$$pK_1' = p\text{H}^+ + pC_{\text{H}_2\text{PO}_4^-} - pC_{\text{H}_3\text{PO}_4} \qquad (3)$$
$$pK_2' = p\text{H}^+ + pC_{\text{HPO}_4^{--}} - pC_{\text{H}_2\text{PO}_4^-} \qquad (4)$$
$$pK_2 = p\text{H}^+ + p\text{HPO}_4^{--} - p\text{H}_2\text{PO}_4^- \qquad (4a)$$
$$pK_3 = p\text{H}^+ + p\text{PO}_4^{---} - p\text{HPO}_4^{--} \qquad (5)$$

pK_2' and $\gamma_{\text{HPO}_4^{--}}$ in dilute solutions are taken as given by the relations

$$pK_2' = pK_2 - \frac{1.5\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad (6)$$
$$-\log \gamma_{\text{HPO}_4^{--}} = \frac{2.0\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad (7)$$

TABLE I

IONIZATION CONSTANTS OF PHOSPHORIC ACID

	25°	37.5°		25°	37.5°
pK_1	...	....	pK_1' (μ = 0.16)	1.94	2.04
pK_2	7.127	7.058	pK_2' (μ = 0.16)	6.680	6.589
pK_3	12.30	12.66[11]			

The third ionization constant is not known accurately but pK_3 enters into our calculations only in the form of an additive constant, since no measurements have been made in the region of P_H in which the tertiary phosphate ion is an appreciable fraction of the total phosphate concentration. Any alteration in the value of pK_3 chosen would simply necessitate a change in the value of pS_3 according to the equation

$$pS_3 = 3p\text{Pb}^{++} + 2p\text{HPO}_4^{--} - 2p\text{H}^+ + 2pK_3 \qquad (8)$$

which is derived by combining Equations 2 and 5.

---

[11] Sendroy and Hastings, *J. Biol. Chem.*, **71**, **783** (1926–27).

Equation 1 similarly can be stated in a logarithmic form

$$pS_2 = p\text{Pb}^{++} + p\text{HPO}_4^{--} \tag{9}$$

Solubilities of the Tertiary Phosphate.—Measurements of the solubility of $Pb_3(PO_4)_2$ have been carried out at 25 and 37.5° in dilute solutions and at an ionic strength of 0.16.

The solutions which the lead phosphate was allowed to saturate contained in all these experiments 0.005 M phosphate, a value which remained constant throughout the time of saturation.

This phosphate concentration was attained by mixing solutions of KH_2PO_4 and Na_2HPO_4 in various proportions, so that the PH might be varied. It was found that during saturation the PH values of the solutions changed, and always in an acid direction. We have no explanation to offer for this change, which sometimes amounted to 0.2; it was, however, a slow effect and the PH was sensibly constant for a long enough time for saturation to take place under definite conditions. The constancy of the phosphate concentration shows that no transformation of the solid phase to or from secondary phosphate could be taking place, since in this process, $Pb_3(PO_4)_2 + H_3PO_4 \rightleftharpoons 3PbHPO_4$, the phosphate concentration would decrease or increase, respectively.

The solubilities observed are hence really those of the tertiary phosphate, a conclusion supported by the sensible constancy of the calculated values of pS_3 over a range of PO_4^{---} concentration of more than twenty times.

TABLE II

SOLUBILITY DATA IN DILUTE SOLUTIONS

Solid phase, $Pb_3(PO_4)_2$; C, phosphate, 0.005 M

No.	pH	pPb$^+$	μ (approx.)	No.	pH$^+$	pPb$^+$	μ (approx.)
	Temp., 25°				Temp., 37.5"		
1	7.194	8.819	0.0117	5	7.136	8.507	0.0117
2	6868	8.539	.0100	6	6.795	8.177	.0100
3	6.692	8.326	.0083	7	6.639	7.984	.0083
4	6.346	7.927	.0070	8	6.261	7.580	.0070

The data obtained in dilute solutions are given in Table II. The values of μ are calculated from the initial composition of the solutions.

The calculation of pS_3 from these data is indicated in Table III. pK'_2 is obtained from Equation 6, and Equation 4 is then used to calculate the

TABLE III

CALCULATION OF pS_3 IN DILUTE SOLUTIONS

No.	$\gamma_{HPO_4^{--}}$	$p\text{HPO}_4^{--}$	$p\text{PO}_4^{---}$	pS_3	No.	$\gamma_{HPO_4^{--}}$	$p\text{HPO}_4^{--}$	$p\text{PO}_4^{---}$	pS_3
		Temp., 25°					Temp., 37.5°		
1	0.65	2.697	7.803	42.06	5	0.65	2.693	8.237	42.00
2	.67	2.845	8.277	42 17	6	.67	2 847	8.732	41.99
3	.69	2.948	8556	42.09	7	.69	2928	8.969	(41.89)
4	.71	3.203	9 157	42.10	8	.71	3.216	9.635	42.01

ratio $C_{\mathrm{HPO_4^{--}}}/C_{\mathrm{H_2PO_4^-}}$. The total phosphate concentration being known, $C_{\mathrm{HPO_4^{--}}}$ is obtained.

$\gamma_{\mathrm{HPO_4^{--}}}$ is calculated by the use of Equation 7 and hence $p\mathrm{HPO_4^{--}}$ obtained. $p\mathrm{PO_4^{---}}$ is then derived from Equation 5, or alternatively pS is derived directly from Equation 8.

The mean values for pS_3 derived (omitting the bracketed value) are 42.10 at 25" and 42.00 at 37.5°.

A set of measurements similar to those in dilute solutions have been made at an ionic strength of 0.16. Solutions of alkali phosphates were raised to this ionic strength by addition of sodium chloride. The data obtained are given in Table IV.

TABLE IV

SOLUBILITY DATA AT $\mu = 0.16$

Solid phase, $Pb_3(PO_4)_2$; C, phosphate, 0.005 M

No.	$p\mathrm{H}^+$	$p\mathrm{Pb}^{++}$	No.	$p\mathrm{H}^+$	$p\mathrm{Pb}^{++}$
	Temp., 25°			Temp., 37.5°	
9	7.015	8.460	13	6.887	8.081
10	6.774	8.243	14	6.719	7.905
11	6.429	7.917	15	6.317	7.518
12	6.202	7.584	16	6.173	7.265

Values of pK_2' for $\mu = 0.16$ are given in Table I. The ratio $C_{\mathrm{HPO_4^{--}}}/C_{\mathrm{H_2PO_4^-}}$ is calculated with the aid of Equation 4 and the observed PH. $C_{\mathrm{HPO_4^{--}}}$ is next obtained. We leave $\gamma_{\mathrm{HPO_4^{--}}}$ indeterminate for the present and hence derive values for $(pS_3 + 2 \log \gamma_{\mathrm{HPO_4^{--}}})$ given in Table V.

TABLE V

CALCULATION OF $(pS_3 + 2 \log \gamma_{\mathrm{HPO_4^{--}}})$, $\mu = 0.16$

No.	$(p\mathrm{HPO_4^{--}} + \log \gamma_{\mathrm{HPO_4^{--}}})$	$(p\mathrm{PO_4^{---}} + \log \gamma_{\mathrm{HPO_4^{--}}})$	$(pS_3 + 2 \log \gamma_{\mathrm{HPO_4^{--}}})$	No.	$(p\mathrm{HPO_4^{---}} + \log \gamma_{\mathrm{HPO_4^{--}}})$	$(p\mathrm{PO_4^{---}} + \log \gamma_{\mathrm{HPO_4^{--}}})$	$(pS_3 + 2 \log \gamma_{\mathrm{HPO_4^{--}}})$
	Temp., 25°				Temp., 37.5°		
9	2.466	7.743	40.87	13	2.478	7.531	40.74
10	2.558	8.076	40.88	14	2.542	7.767	40.69
11	2.745	8.608	40.97	15	2.759	8.382	40.76
12	2.904	8.994	40.74	16	2.858	8.625	(40.49)

The mean values for $(pS_3 + 2 \log \gamma_{\mathrm{HPO_4^{--}}})$ derived are 40.86 at 25° and 40.73 at 37.5°. Hence, from the values of pS_3 already obtained, $-\log \gamma_{\mathrm{HPO_4^{--}}}$ has a value of about 0.62 at 25° and 0.635 at 37.5'.

Thus in the solutions of $\mu = 0.16$, $\gamma_{\mathrm{HPO_4^{--}}}$ has the value 0.24 (25°) and 0.23 (37.5"). Making use of the values of pK_2 and pK_2' ($\mu = 0.16$) given in Table I, it can be calculated that $\gamma_{\mathrm{H_2PO_4^-}}$ has values of about 0.67 and 0.68 at 25 and 37.5". These values have already been shown[6] to agree with data obtained for pK_1 and pK_1' ($\mu = 0.16$). Thus it can be concluded that the two sets of data on the solubility of tertiary lead phosphate are in good agreement.

Solubilities **of** the Secondary Phosphate.—In an attempt to obtain the solubility product of $PbHPO_4$, a series of solutions similar to those above described ($\mu = 0.16$) and initially at similar *PH* values were saturated with solid $PbHPO_4$. It was observed, however, that the phosphate content of the solutions increased and the *PH* fell much more than was the case when the tertiary phosphate was the solid phase. There was thus reason to consider that the reaction $3\ PbHPO_4 \longrightarrow Pb_3(PO_4)_2 + H_3PO_4$ was taking place, and it appeared doubtful whether the solution would be truly saturated with $PbHPO_4$ or whether its lead-ion content would show a value intermediate between those corresponding to the solubilities of $PbHPO_4$ and $Pb_3(PO_4)_2$.

The observed phosphate concentrations were from 0.0057 to 0.0081 molar, the *PH* values ranged from 5.61 to 6.36, and the values of (pPb^{++} + pHPO$_4^{--}$) were 11.40–11.64 at 25° and 11.16–11.29 at 37.5'. The lead-ion activities were higher than those corresponding to the solubility of $Pb_3(PO_4)_2$. The ionic product for the secondary phosphate was not, however, a constant, and we concluded that experiments should be undertaken under conditions where the secondary phosphate was the more stable salt. Such conditions were attained by employing *PH* values in the region 2.0–2.5.

As before, four solutions were studied at each temperature, mixtures of KH_2PO_4 and HCl being made and their ionic strength raised to the value 0.16 by adding sodium chloride. The data and calculation of pS_2 are given in Table VI. From the observed *PH* and phosphate concentrations, pH$_2$PO$_4^-$ is calculated, using the values of pK_1' given in Table I, the values of $\gamma_{H_2PO_4^-}$ obtained in the last section and Equation 3. pHPO$_4^{--}$ is then obtained using the values of pK_2 given in Table I and Equation 4a.

TABLE VI

SOLUBILITIES OF $PbHPO_4$, $\mu = 0.16$

Temp.. °C.	pH$^+$	pPb^{++}	C, phosphate	pH$_2$PO$_4^-$	pHPO$_4^{--}$	pS_2
25	2.515	3.508	0.0320	1.770	6.382	9.89
	2.303	3.278	.0336	1.803	6.627	9.90
	2.494	3.345	.0173	2.042	6.675	10.02
	2.301	2.885	.0176	2.085	6.911	9.80
37.5	2.341	3.125	.0326	1.829	6.546	9.67
	2.156	2.763	.0344	1.876	6.778	9.54
	2.426	2.925	.0173	2.078	6.710	9.64
	2.067	2.438	.0181	2.196	7.187	9.62

The mean values derived for pS_2 are 9.90 at 25° and 9.62 at 37.5'. It can readily be calculated from the values of pS_3 previously obtained that the solubility of $Pb_3(PO_4)_2$ in the above solutions is greater than that observed for $PbHPO_4$. Thus the latter is the stable salt in these solutions.

From the values of pS_2 at the two temperatures it can be calculated that the heat of solution of $PbHPO_4$ at infinite dilution is about $-10{,}000$ cal. In view of the uncertainty in pK_3 it is not worth while to calculate a value for the heat of solution of $Pb_3(PO_4)_2$.

Equilibrium Conditions

The conditions under which both $PbHPO_4$ and $Pb_3(PO_4)_2$ will be in equilibrium with a solution can now be defined. The condition takes the form

$$\frac{S_2}{am\sim.--} = \frac{S_3^{1/3}}{a;<,---}$$

It may also be stated in the forms

$$a^2_{H^+} \times a_{HPO_4^{--}} = \frac{K_3^2\,S_2^3}{S_3}$$

$$a_{H^+} \times a_{H_2PO_4^-} = \frac{K_3^2\,S_2^3}{K_2\,S_3}$$

Numerical values are given in Table VII.

TABLE VII

EQUILIBRIUM CONDITIONS FOR $PbHPO_4$ AND $Pb_3(PO_4)_2$

	25°	37.5°
$a^2_{H^+} \times a_{HPO_4^{--}}$	$10^{-12.20}$	$10^{-12.18}$
$a_{H^+} \times a_{H_2PO_4^-}$	$10^{-5.07}$	$10^{-5.12}$

The conditions are very similar at both temperatures. The higher the phosphate concentration the lower the hydrogen-ion activity at equilibrium. Thus with M phosphate the $p\mathrm{H}^+$ is about 5, with $M/1000$ phosphate the pH+ is about 2.

This latter phosphate concentration is of the same order as is found in blood and in animal tissues, of which the $p\mathrm{H}^+$ is about 7.0–7.3. Thus under these conditions $Pb_3(PO_4)_2$ is definitely the stable phosphate of lead and the statement[2] that a slight shift to the acid side converts it to $PbHPO_4$ is quite erroneous. This statement was based on arguments physicochemically unsound.

Making use of the data obtained, the solubilities in (human) blood serum will now be calculated. The activity coefficients are assumed to be the same in serum as in 0.16 M sodium chloride. For low concentrations of lead salts in the latter solution $\gamma_{Pb^{++}}$ was found to be 0.17. The pH+ of serum is about 7.33, and its phosphate concentration about 1.2×10^{-3} molar. Hence it is calculated that the lead-ion concentration in serum saturated at 37.5° with $Pb_3(PO_4)_2$ is 5.5×10^{-8}, while the solubility of $PbHPO_4$ is much greater, namely, 6.3×10^{-6} molar.

In order to be able to calculate solubilities of $PbHPO_4$ and $Pb_3(PO_4)_2$ under various conditions in terms of lead-ion *concentrations* from the values obtained for pS_2 and pS_3, it is necessary to be able to evaluate $\gamma_{Pb^{++}}$. Data obtained by one of the authors, which will be published elsewhere,[12]

---

[12] **Millet,** *Trans. Faraday Soc.*, 25, (1929).

show that $\gamma_{Pb^{++}}$ is given fairly accurately by the Debye-Hückel expression in solutions of alkali chlorides up to 0.16 M.

Summary

Solubilities of $Pb_3(PO_4)_2$ and $PbHPO_4$ in aqueous solutions have been measured, lead-ion activities being determined with the lead electrode. The values of the solubility products deduced are as follows: $S_2 = a_{Pb^{++}} \times a_{HPO_4^{--}} = 10^{-9.90}$ at 25°; $10^{-9.62}$ at 37.5°. $S_3 = a^3_{Pb^{++}}$ X $a^2_{PO_4^{---}} = 10^{-42.10}$ at 25°, $10^{-42.00}$ at 37.5°, when K_3 (the third ionization constant of phosphoric acid) is taken to have the values $10^{-12.30}$ at 25° and $10^{-12.66}$ at 37.5".

The conditions for equilibrium between the two salts are discussed and the biological bearing of the work is mentioned. $Pb_3(PO_4)_2$ is the more stable salt under body conditions.

LIVERPOOL, ENGLAND

[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY, UNIVERSITY OF LIVERPOOL]

THE IONIZATION CONSTANTS OF PHOSPHORIC ACID[1]

BY MAURICE JOWETT AND HORACE MILLET

RECEIVED AUGUST 20, 1928 PUBLISHED APRIL 5, 1929

In the course of an investigation[2] on the solubilities of the secondary and tertiary phosphates of lead, it became evident that the values available in the literature for the ionization constants of phosphoric acid were insufficient for the purpose of that work.

We therefore have made measurements to determine the first ionization constant at 25 and 37.5". A few measurements bearing on the second ionization constant are also reported. Relevant data of other observers are also considered and a value is derived for the third ionization constant. The activity concept is made use of throughout.

Methods

Measurements of hydrogen-ion activity were made by means of cells in which a quinhydrone electrode was connected with a normal calomel electrode by a bridge of saturated potassium chloride solution. This bridge is assumed to eliminate liquid–liquid P. D's.

At 25° the P_H is obtained by means of the relation[3]

$$pH^+ = \frac{0.4136 - E}{0.05911}$$

---

[1] This investigation was undertaken on behalf of the Liverpool Medical Research Organization, Professor W. Blair Bell, Director, University of Liverpool.

[2] Millet and Jowett, THIS JOURNAL, 51, 997 (1929).

[3] Millet, *Trans. Faraday Soc.*, 23, 521 (1927).

where E, the e.m.f. of the cell, is positive when the quinhydrone electrode is the positive element.

The corresponding formula for 37.5° is[4]

$$pH^+ = \frac{0.4068 - E}{0.06160}$$

When the solutions have a high electrolyte concentration, a correction must be made for the so-called neutral salt error of the quinhydrone electrode. The corrections for an ionic strength of 0.16 have been taken by us as $\Delta pH^+ = -0.008$ at 25°[5] and $\Delta pH^+ = -0.006$ at 37.5°.[6] The hydrogen electrode standard is that of G. N. Lewis, Brighton and Sebastian.[7]

The e.m.f. measurements were carried out in duplicate. Solutions were made up at room temperature from recrystallized salts. No correction has been made for the expansion of the solutions with rising temperature.

The First Ionization Constant.—The first ionization constant of phosphoric acid, K_1, is defined by the relation

$$pK_1 = pH^+ + pH_2PO_4^- - pH_3PO_4 \qquad (1)$$

where pX denotes the negative logarithm of the activity of the chemical species X. It is also useful to define a quantity K_1' by the relation

$$pK_1' = pH^+ + pC_{H_2PO_4^-} - pC_{H_3PO_4} \qquad (2)$$

where pC_X denotes the negative logarithm of the concentration of the chemical species X.

Older work has not been calculated in terms of the activity concept, with the exception of the conductivity measurements of Noyes and Eastman at 18° given by Abbott and Bray,[8] which Sendroy and Hastings[9] state to fit the relation

$$pK_1' = 2.11 - 0.5\sqrt{\mu}$$

μ being the ionic strength.

The e.m.f. data of Ringer[10] do not lead to a definite value for pK_1, when calculated according to activity theory.

Measurements in Dilute Solutions.—Solutions were made up by diluting mixtures of decimolar KH_2PO_4 and decinormal HCl. The stoichiometric composition of the solutions and the PH values obtained are given in Table I.

---

[4] Corran and W. C. M. Lewis, *Biochem. J*, **18**, 1358 (1924).

[5] *Sorensen, Sörensen and Lang, Ann. chim.,* [9] **16**, 283 (1921).

[6] *P. S. Lewis, Biochem. J., 20,* 986 (1926).

[7] *G. N. Lewis,* Brighton *and Sebastian,* THIS JOURNAL, **39**, 2245 (1917); W. M. Clark, *"Determination of Hydrogen Ions," 2d ed., Williams and Wilkins Co., Baltimore, Md.,* **1923**, p. 285.

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

[9] *Sendroy and Hastings, J. Biol. Chem.,* **71**, 783 (1926–27).

[10] *Ringer, Chem. Weekblad, 6,* 446 (1909).

TABLE I

COMPOSITION AND PH VALUES OF DILUTE SOLUTIONS

No.	Composition KH_2PO_4, *M*	HCl, *M*	PH values from quinhydrone elec.	No.	Composition KH_2PO_4, *M*	HCl, *M*	PH values from quinhydrone elec.
	Temp., 25°				Temp., 37.5"		
1	0.015	0.005	2.703	6	0.01667	0.010	2.406
2	.0225	.0065	2.675	7	.0225	.0065	2.718
3	.030	.008	2.667	8	.025	.009	2.578
4	.045	.011	2.652	9	.0375	.0195	2.307
5	.061	.014	2.651				

In order to calculate values of pK_1 from the above data, we must evaluate γ_{H^+} and $\gamma_{H_2PO_4^-}$, the activity coefficients of hydrogen ion and the primary phosphate ion. Since the solutions are not very concentrated, approximate relationships will be reasonably accurate.

According to Brönsted,[11] in solutions of hydrochloric acid and potassium chloride up to 0.1 molar the following relations hold good

$$-\log \gamma_{H^+}\gamma_{Cl^-} = 0.90\sqrt{\mu} - \mu$$
$$-\log \gamma_{K^+}\gamma_{Cl^-} = \sqrt{\mu} - 0.8\mu$$

Hence, assuming that $\gamma_{K^+} = \gamma_{Cl^-}$ and that γ_{Cl^-} is the same in corresponding solutions of potassium chloride and hydrochloric acid, we derive the equation

$$-\log \gamma_{H^+} = 0.4\sqrt{\mu} - 0.6\mu \qquad (3)$$

which is assumed to hold for the present cases.

Cohn,[12] working with mixtures of KH_2PO_4 and K_2HPO_4, was able to represent the activity coefficient of the primary phosphate ion by the relation

$$-\log \gamma_{H_2PO_4^-} = \frac{0.5\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad (4)$$

which we likewise take as valid for the systems we are considering.

From the PH value, Equation 3 allows us to calculate C_{H^+}, a value for μ being assumed and subsequently replaced by a more accurate one. $C_{H_2PO_4^-}$ is then obtained from the principle of electrical equivalence ($C_{H_2PO_4^-} = C_{H^+} + C_{K^+} - C_{Cl^-}$), and $pH_2PO_4^-$ calculated with the use of Equation 4. $C_{H_3PO_4}$ is obtained by subtracting $C_{H_2PO_4^-}$ from the total phosphate concentration. Up to the present point we have no basis for any value for γH_3PO_4, which is left indeterminate.

Values of $pK_1 - \log \gamma_{H_3PO_4}$ are calculated in Table II. To save space, values of γ_{H^+} and $\gamma_{H_2PO_4^+}$ are omitted; they range from 0.908 to 0.868, and 0.882 to 0.810, respectively. The numbers refer to the solutions given in Table I.

The above values of $pK_1 - \log \gamma_{H_3PO_4}$ show no trend with concentration and hence we take $\gamma_{H_3PO_4} = 1$, and derive values for pK_1 at 25° of 2.10, and at 37.5° of 2.16.

---

[11] Bronsted, *Trans. Faraday Soc*, 23, 419 (1927).

[12] Cohn, THIS JOURNAL, 49, 173 (1927).

TABLE II

CALCULATION OF pK_1 IN DILUTE SOLUTIONS

Temp., °C.	No.	μ	C_{H^+}	$C_{H_2PO_4^-}$	$C_{H_3PO_4}$	$pK_1 - \log \gamma_{H_3PO_4}$
25	1	0.017	0.00218	0.01218	0.00282	2.122
	2	.025	.00236	.01836	.00414	2.092
	3	.0325	.00243	.02443	.00557	2.096
	4	.0475	.00255	.03655	.00845	2.098
	5	.0635	.00258	.04958	.01142	2.105
37.5	6	.021	.00435	.01102	.00565	2.176
	7	.025	.00214	.01814	.00436	2.163
	8	.028	.00297	.01897	.00603	2.147
	9	.043	.00562	.02362	.01388	2.156

Britton's data[13] obtained by electrometric titration of phosphoric acid with caustic soda at 20°, using the hydrogen electrode, have been recalculated by us on the same basis as our own data, the mean value of pK_1 deduced being 2.01. This is lower than the value 2.08, which would be derived at 20° from our values at 25 and 37.5° if a constant temperature coefficient were assumed, and lower than the value calculated by Sendroy and Hastings for 18°, namely, 2.11.

Measurements at Total Ionic Strength 0.16.—For the purpose of the investigation already referred to,[2] values of pK_1' at an ionic strength of 0.16 were required. Solutions of similar composition to those already used were made up, sodium chloride being added to raise the ionic strength to approximately 0.16.

Since no suitable value for γ_{H^+} was available in the literature, γ_{H^+} was measured for a solution containing 0.01 *M* HCl and 0.15 M NaCl.

TABLE III

COMPOSITION AND PH VALUES OF SOLUTIONS (μ = 0.16)

No.	KH_2PO_4, M	HCl, M	NaCl, *M*	*Pa* (25°)	*PH* (37.5°)
1	0.03	0.0053	0.1281	2.825	2.885
2	.03	.0080	.1270	2.607	2.659
3	.03	.0120	.1252	2.407	2.466
4	.03	.0176	.1224	2.194	2.255

TABLE IV

CALCULATION OF pK_1' AND pK_1 (μ = 0.16)

Temp, °C.	No.	C_{H^+}	$C_{H_2PO_4^-}$	$C_{H_3PO_4}$	pK_1'	pK_1
25	1	0.00166	0.02636	0.00364	1.965	2.138
	2	.00275	.02475	.00525	1.934	2.107
	3	.00435	.02235	.00765	1.941	2.114
	4	.00711	.01951	.01049	1.925	2.098
37.5	1	.00143	.02613	.00387	2.056	2.222
	2	.00241	.02441	.00559	2.019	2.185
	3	.00376	.02176	.00824	2.044	2.210
	4	.00611	.01851	.01149	2.048	2.214

---

[13] Britton, *J. Chem. Soc.*, 1927, 614.

The value found was 0.90 at 25° and 0.91 at 37.5°, and this was taken as valid for the solutions of which the PH was measured, the composition of which is given in Table III.

The value of pK_1' obtained is 1.94 at 25° and 2.04 at 37.5°. The values of pK_1, 2.11 and 2.21, have been calculated from values of $\gamma_{H_2PO_4^-}$ deduced elsewhere,[2] namely 0.67 and 0.68.

The agreement of these values of pK_1 with those obtained in more dilute solutions is sufficiently good to confirm the conclusion that $\gamma_{H_3PO_4}$ does not depart appreciably from a value of unity.

The Second Ionization Constant.—Many measurements have been made of the PH values of mixtures of the primary and secondary alkali phosphates but the majority are unsuitable for the accurate evaluation of the second ionization constant of phosphoric acid, K_2, since the ionic strengths of the systems investigated are too high.

K_2 may be defined by the relation $pK_2 = pH^+ + pH_2PO_4^- - pHPO_4^{--}$ and the quantity pK_2' is defined similarly to pK_1'.

Cohn[12] has, however, recently made an extensive investigation of mixtures of primary and secondary phosphates at 18°, and this author's measurements, which are in concordance with those of Sorensen and Michaelis, lead to a value of pK_2 which is probably very accurate. Reduced to the G. N. Lewis standard for the hydrogen electrode, this value is 7.130.

For other temperatures no values of any great accuracy appear to be available. Sendroy and Hastings[g] state that unpublished measurements at 20° give a value of about 7.18, and suggest that the value at 38° may be 7.15.

We have made a number of measurements of the PH of mixtures containing 0.0025 M KH_2PO_4 and 0.0025 M Na_2HPO_4 ($\mu = 0.01$). The mean values obtained are 6.997 at 25° and 6.928 at 37.5°, probably accurate to about 0.003 pH^+. From these values, using Cohn's relation

$$pK_2 = pK_2' + \frac{1.5\sqrt{\mu}}{1 + 1.5\sqrt{\mu}}$$

pK_2 is calculated to be 7.127 at 25° and 7.058 at 37.5'. The value at 25° is close to the value 7.130 obtained by Cohn at 18°.

The data of Michaelis and Garmendia[14] for the three most dilute solutions measured, when similarly calculated and reduced to the G. N. Lewis standard, give a value for pK_2 at 25° of about 7.11. Britton's data[13] on the same basis give a value of about 7.04 at 20°.

Measurements made by us on mixtures containing 0.0025 M KH_2PO_4 and 0.0025 M Na_2HPO_4, of which the ionic strength was raised to 0.16 with NaCl, gave pH^+ (and also pK'_2) values of 6.680 at 25° and 6.589 at 37.5°.

---

[14] Michaelis and Garmendia, *Biochem. Z.*, **67**, 431 (1914).

The Third Ionization Constant.—Sendroy and Hastings[9] have made PH measurements at 38° on mixtures of secondary and tertiary phosphates and found that pK'_3 could be represented approximately by the relation

$$pK'_3 = 12.66 - 2.25\sqrt{\mu}$$

pK_3 and pK'_3 are defined in a manner similar to pK_1 and pK'_1. As the data used lie between the limits $\sqrt{\mu} = 0.25$ and $\sqrt{\mu} = 0.50$, the extrapolation to infinite dilution is somewhat uncertain.

Suitable data for the calculation of pK_3 at other temperatures are scanty. Prideaux and Ward's measurements[15] were made at ionic strengths of 0.085 upward. Kolthoff's measurements[16] were also made at high ionic strengths; by a method not clearly explained this author calculates pK_3 at 18" to be about 12.30.

The electrometric titrations of Britton[13] at 20°, however, were carried out in the range $\mu = 0.033$ to $\mu = 0.047$, and the values obtained may be used in attempting to evaluate pK_3.

No very satisfactory basis is available for calculating the required activity coefficients—γ_{OH^-}, $\gamma_{H_2PO_4^{--}}$ and $\gamma_{PO_4^{---}}$.

As an approximate relation we have made use of an equation analogous to that used by Sendroy and Hastings

$$-\log y = 0.45\, n^2 \sqrt{\mu}$$

K_w has been taken as 0.68×10^{-14}. To Britton's PH values 0.04 has been added to correct them to the G. N. Lewis standard.

Then pK_3 is defined by the relation

$$pK_3 = pH^+ + pC_{PO_4^{---}} - pC_{H_2PO_4^{--}} + 2.25\sqrt{\mu}$$

From PH and γ_{OH^-}, C_{OH^-} is evaluated, and $C_{PO_4^{---}}$ and $C_{H_2PO_4^{--}}$ obtained from the principle of electrical equivalence.

Values at either end of the series have been omitted as being less accurate. The mean value of pK_3 obtained is 12.11. It should be noted that Britton's data give values for pK_1 and pK_2 about 0.1 lower than do other data. An additional error of the same order may be introduced into pK_3 owing to our having used a tentative formula for the activity coefficients. Thus the value 12.11 may be in error by 0.1–0.2. Sendroy and Hastings' value of 12.66 at 38" may be in error to a similar extent. Thus the temperature coefficient is a doubtful quantity, but a value of 12.3 might be interpolated for 25".

Heats of Ionization of Phosphoric Acid.—The heats of ionization of phosphoric acid, as far as the first two stages are concerned, may be calculated as follows from the values of pK_1 and pK_2 obtained in this paper.

---

[15] Prideaux and Ward, *J. Chem. Soc.*, **125**, 429 (1924).

[16] I. M. Kolthoff, *Rec. trav. chim.*, 46, 350 (1927).

Reaction	pK (25°)	pK (37.5°)	Heat evolved
$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$	2.10	2.16	+2000
$H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$	7.127	7.058	−2300

The calculated heats of ionization, which are in calories per mole, refer, of course, to the ionization at infinite dilution.

The values of pK_3 calculated are insufficiently accurate for the heat effect of the third ionization step to be calculated. Heat, however, is evolved in this ionization.

Summary

With the quinhydrone electrode measurements of the *P*H values of phosphate mixtures have been made which lead to the following values for the ionization constants of phosphoric acid

$$pK_1\ (25^\circ) = 2.10,\quad pK_1\ (37.5^\circ) = 2.16$$
$$pK_2\ (25^\circ) = 7.13,\quad pK_2\ (37.5^\circ) = 7.06$$

These figures are compared with those derived from other data.

From the data of Britton pK_3 at 20° is calculated to be about 12.1.

Liverpool, England

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 192]

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

By Linus Pauling

Received September 5, 1928 Published April 5, 1929

1. The Relative Stability of Alternative Structures of Ionic Crystals.—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate, $Al_2SiO_4F_2$, crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Efforts to provide such a treatment for simple alternative structures, such as the sodium chloride and cesium chloride structures and the fluoride and rutile structures, have been made with the aid of the Born potential expression and modifications of it, Assuming that all ions repel each other according to a high inverse power of the distance between them (the repulsive potential being proportional to r^{-n}), the equilibrium energy of a crystal is given by

$$\Phi = -\frac{z^2e^2A}{R}\left(1 - \frac{1}{n}\right) \tag{1}$$

in which R is the equilibrium distance between two adjacent ions in the crystal, and A is the Madelung constant characteristic of the structure. A knowledge of how R changes from structure to structure for a given substance would then allow the prediction of which structure is stable, if Equation 1 were accurate. Methods of calculating R have been suggested.[1] It is found, however, that Equation 1 is in error by at least 2% in some cases,[1b] and this error of around 5000 cal./mole suffices to invalidate the theory in applications of this kind. An explanation of the sodium chloride–cesium chloride transition which accounts for the observed properties of the alkali halides has been reported,[2] but the considerations involved (including deformation phenomena) have not yet been given quantitative formulation.

The application of these methods to more complex crystals would involve the highly laborious calculation of the Madelung constant for a number of complicated ionic arrangements. Furthermore, the methods provide no way of determining the possible structures for which calculations should be made. An infinite number of possible atomic arrangements for a complicated substance such as a silicate are provided by the theory of space groups. There is desired a set of simple rules, which need not be rigorous in their derivation nor universal in their application, with the aid of which the few relatively stable structures can be identified among the multitude possible for a given substance. These rules could be used in the prediction of atomic arrangements for comparison with x-ray data. They would also provide a criterion for the probable correctness of structures suggested by but not rigorously deduced from experimental measurements. Finally, they would permit the intuitive understanding of the stability of crystals in terms of visualizable interionic interactions.

2. The Application of the Coordination Theory in the Determination of the Structures of Complex Crystals.—As a result of the recent increase in knowledge of the effective radii of various ions in crystals,[3] Professor W. L. Bragg has suggested and applied a simple and useful theory leading to the selection of possible structures for certain complex crystals. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will be determined essentially by the large ions, and may approximate a close-packed arrangement of the large ions alone,

---

[1] (a) F. Hund, *Z. Physik*, **34**, 833 (1925); (b) Linus Pauling, THIS JOURNAL, **50**, 1036 (1928); *Z. Krist.*, **67**, 377 (1928).

[2] Linus Pauling, *ibid.*, **69**, 35 (1928).

[3] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923).

with the small ions tucked away in the interstices in such a way that each one is equidistant from four or six large ions. In some cases not all of the close-packed positions are occupied by ions, and an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known crystal radius (usually oxygen ions with a radius of 1.35–1.40 Å.) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities of reflection of x-rays, the large ions being also shifted somewhat from the close-packed positions if necessary. With the aid of this method Bragg and his co-workers have made a very significant attack on the important problem of the structure of silicates, involving the determination of structures for beryl, $Be_3Al_2Si_6O_{18}$,[4] chrysoberyl, $BeAl_2O_4$,[5] olivine, $(Mg, Fe)_2SiO_4$,[6] chondrodite, $H_2Mg_5Si_2O_{10}$, humite, $H_2Mg_7Si_3O_{14}$, clinohumite, $H_2Mg_9Si_4O_{18}$,[7] phenacite, Be_2SiO_4,[8] etc.

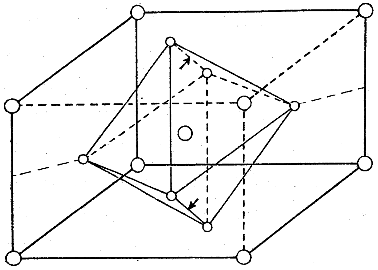


Fig. 1.—The unit of structure for rutile. Large circles represent titanium ions; small circles oxygen ions. An octahedron with a titanium ion at its center and oxygen ions at its corners is shown. The two edges marked with arrows are shared with adjoining octahedra.

During the investigation of the structure of brookite,[9] the orthorhombic form of titanium dioxide, a somewhat different method for predicting possible structures for ionic crystals was developed, based upon the assumption of the coördination of the anions in the crystal about the cations in such a way that each cation designates the center of a polyhedron, the corners of which are occupied by anions. This method leads for a given substance to a small number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the theory further indicates the amount and nature of the distortion from the close-packed arrangement.

The structures of rutile and anatase, the two tetragonal forms of titanium dioxide, have been determined by rigorous methods (Figs. 1 and 2). They seem at first sight to have little in common beyond the fact

[4] W. L. Bragg and J. West, *Proc. Roy. Soc. London*, **111A,** 691 (1926).

[5] W. L. Bragg and G. B. Brown, *ibid.*, **110A,** 34 (1926).

[6] W. L. Bragg and G. B. Brown, *Z. Krist.*, 63, 538 (1926).

[7] (a) W. L. Bragg and J. West, *Proc. Roy Soc. London*, **114A,** 450 (1927); (b) W. H. Taylor and J. West, *ibid.*, **117A,** 517 (1928).

[8] W. L. Bragg, *ibid.*, **113A,** 642 (1927).

[9] Linus Pauling and J. H. Sturdivant, Z. *Krist*, 68,239 (1928).

that each is a coördination structure, with six oxygen atoms about each titanium atom at octahedron corners. From a certain point of view, however, they are closely similar. They are both made up of octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium-oxygen distance is a constant, with the value 1.95–1.96 Å. The basic octahedra are only approximately regular; in each crystal they are deformed in such a way as to cause each shared edge to be shortened from 2.76 Å. (the value for regular octahedra) to 2.50 **if.,** the other edges being correspondingly lengthened.

As a result of these considerations the following assumptions were made: (1) Brookite is composed of octahedra, each with a titanium ion at its center and oxygen ions at its corners. (2) The octahedra share edges and corners with each other to such an extent as to give the crystals the correct stoichiometric composition. **(3)** The titanium-oxygen distances throughout are 1.95–1.96 Å. Shared edges of octahedra are shortened to 2.50 Å.

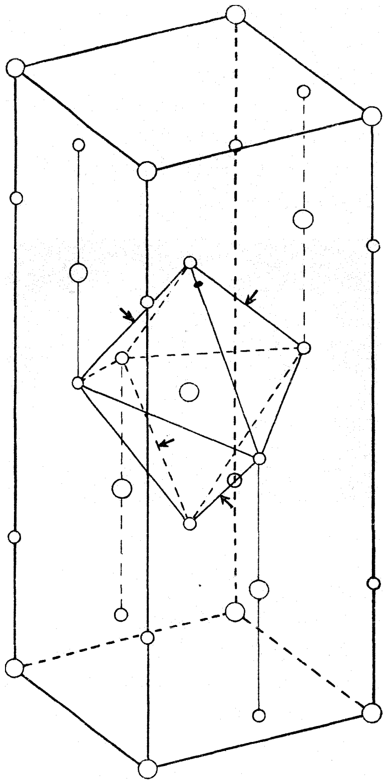


Fig. 2—The unit of structure of anatase. The titanium octahedron shares the four edges marked with arrows with adjoining octahedra.

Two structures satisfying these requirements were built out of octahedra. The first was not the structure of brookite. The second, however, had the same space-group symmetry as brookite (V_h^{15}), and the predicted dimensions of the unit of structure agreed within 0.5% with those observed. Structure factors calculated for over fifty forms with the use of the predicted values of the nine parameters determining the atomic arrangement accounted satisfactorily for the observed intensities of reflections on rotation photographs. This extensive agreement is so striking as to permit the structure proposed for brookite (shown in Fig. 3) to be accepted with confidence.

The method was then applied in predicting the structure of the orthorhombic crystal topaz, $Al_2SiO_4F_2$.[10] It was assumed that each aluminum ion is surrounded by four oxygen ions and two fluorine ions at the corners

[10] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928).

of a regular octahedron, and each silicon ion by four oxygen ions at the corners of a regular tetrahedron. The length of edge of octahedron and tetrahedron was taken as 2.72 Å., corresponding to crystal radii of 1.36 Å. for both oxygen and fluorine ions. One structure was built up of these polyhedra. On studying its distribution of microscopic symmetry elements, it was found to have the space-group symmetry of V_h^{16}, which is that of topaz. Its unit of structure approximates that found experimentally, and the predicted values of the fifteen parameters determining the atomic arrangement account for the observed intensities of reflection from the pinacoids. This concordance is sufficient to make it highly probable that the correct structure of topaz has been found (Fig. 4).[11]

3. The Principles Determining the Structure of Complex Ionic Crystals.—The success of the coordination method in predicting structures for brookite and topaz has led to the proposal of a set of principles governing the structure of a rather extensive class of complex ionic crystals.

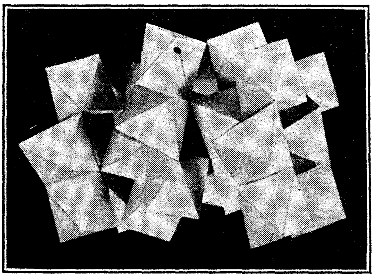


Fig. 3.—The structure of brookite.

The crystals considered are to contain only small cations, with relatively large electric charges, that is, usually trivalent and tetravalent cations, with crystal radii not over about 0.8 Å. All anions are large (over **1.35** Å.) and univalent or divalent. Furthermore, they should not be too highly deformable. The most important anions satisfying this restriction are the oxygen ion and the fluorine ion, with crystal radii 1.35–1.40 Å.[12]

This physical differentiation of the anions and cations under discussion in regard to size and charge finds expression throughout this paper. Markedly different roles are attributed anions and cations in the construction of a crystal; as a result a pronounced distinction between them has been made in the formulation of the structural principles.

Throughout our discussion the crystals will be referred to as composed of ions. This does not signify that the chemical bonds in the crystal arc necessarily ionic in the sense of the quantum mechanics; they should not, however, be of the extreme non-polar or shared electron pair type.[13] Thus compounds of copper[14] and many other eighteen-shell atoms cannot be

---

[11] Professor W. L. Bragg has written the author that the same ideal structure has been found by J. West (paper to be published in the *Proceedings of the Royal Society).*

[12] The crystal radii used in this paper are those of Pauling, THIS JOURNAL, *49,765 (1927).*

[13] (a) P. London, Z. *Physik,* 46,455 *(1928);* (b) L. Pauling, *Proc. Nat. Acad. Sci., 14, 359 (1928).*

[14] **Such** as $K_2CuCl_4{\cdot}2H_2O$, whose structure has been determined by S. B Hendricks and R. G Dickinson, THIS JOURNAL, *49,2149 (1927).*

treated in this way. Shared electron pair bonds are also present in complexes containing large atoms with a coordination number of four, such as the molybdate ion, $[MoO_4]^{--}$, the arsenate ion, $[AsO_4]^{--}$, etc.

The principles described in the following six sections have been deduced in part from the empirical study of known crystal structures and in part from considerations of stability involving the crystal energy.

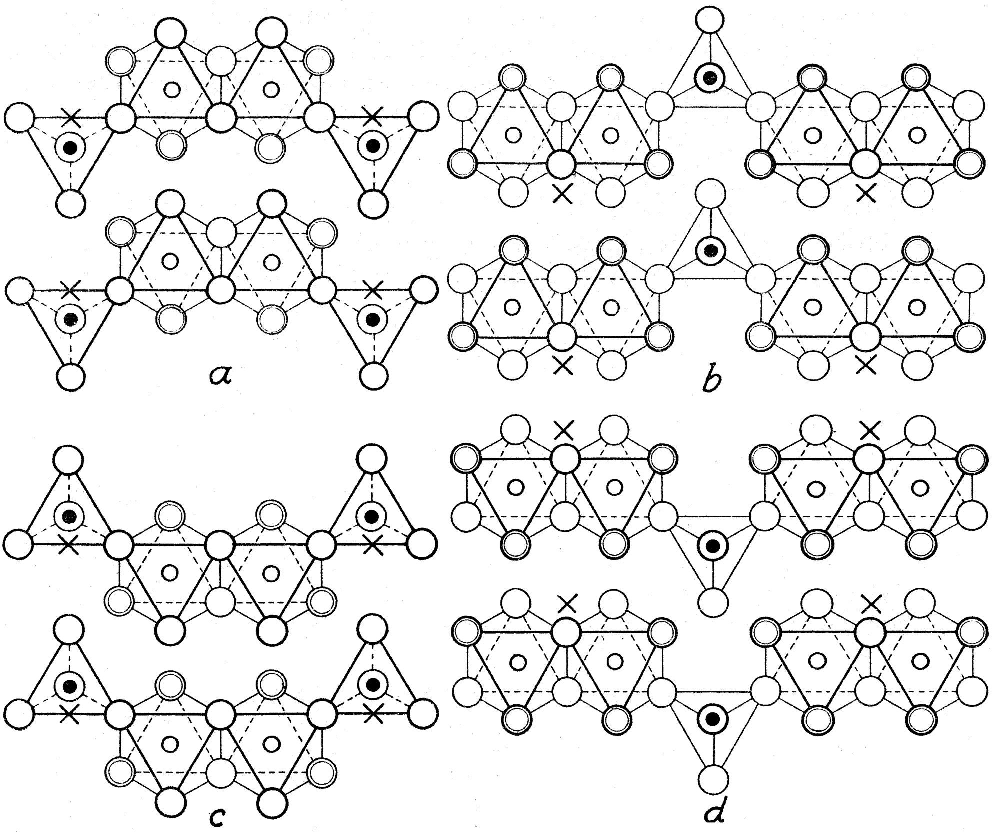


Fig. 4.—The structure of topaz. The layers are to be superposed in the order *abcd*, with *d* uppermost. The crosses are the traces of the corners of the unit of structure in the plane of the paper. Large circles represent oxygen, large double circles fluorine, small open circles aluminum, and small solid circles silicon ions.

4. The Nature of the Coordinated Polyhedra.—I. A *coordinated polyhedron of anions is formed about each cation, the cation–anion distance being determined by the radius sum and the coördination number of the cation by the radius ratio.*

In the case of crystals containing highly charged cations the most important terms in the expression for the crystal energy are those representing the interaction of each cation and the adjacent anions. The next terms in importance are those representing the mutual interaction of the anions. The negative Coulomb energy causes each cation to attract to itself a number of anions, which approach to the distance at which the Coulomb attraction is balanced by the characteristic cation–anion repulsive forces. This distance is given with some accuracy by the sum of the crystal radii of cation and anion.[12]

If too many anions are grouped about one cation, the anion–anion repulsion becomes strong enough to prevent the anions from approaching this closely to the cation. The resultant increase in Coulomb energy causes such a structure to be unstable when the anion–cation distance is increased to a value only slightly greater than the radius sum. Approximate lower limits of the radius ratio (the ratio of cation radius to anion radius) leading to a stable structure with given coordination number can accordingly be calculated purely geometrically.[15,12] The minimum radius ratios for tetrahedra, octahedra and cubes are given in Table I.

TABLE I

RADIUS RATIOS AND COORDINATION NUMBERS

Polyhedron	Conrdination number	Minimum radius ratio
Tetrahedron	4	$\sqrt{3}/\sqrt{2} - 1 = 0.225$
Octahedron	6	$\sqrt{2} - 1 = 0.414$
Cube	8	$\sqrt{3} - 1 = 0.732$

Since the repulsive forces are determined by the true sizes of ions, and not their crystal radii, the radius ratios to be used in this connection are the ratios of the univalent cation radii to univalent anion radii.[12] Values of this ratio for small ions are given in Table II, together with predicted and observed coordination numbers, the agreement between which is excellent.

TABLE II

COÖRDINATION NUMBERS FOR IONS IN OXIDES

Ion	Radius ratio	Predicted coordination number	Observed coordination number	Strength of electrostatic bonds
B^{+++}	0.20	3 or 4	3 or 4	1 or $^3/_4$
Be^{++}	.25	4	4	$^1/_2$
Li^{+}	.34	4	4	$^1/_4$
Si^{++++}	.37	4	4	1
Al^{+++}	.41	4 or 6	6	$^3/_4$ or $^1/_2$
Mg^{++}	.47	6	6	$^1/_3$
Ti^{++++}	.55	6	6	$^2/_3$
Sc^{+++}	.60	6	6	$^1/_2$
Mo^{++++++}	.53	6	6	1
Nb^{+++++}	.57	6	6	6
Zr^{++++}	.62	6	6 or 8	$^2/_3$ or $^1/_2$

---

[15] Such calculations were first made and substantiated by comparison with observed structures in some cases by V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Oslo, 1927.

The radius ratio for B^{+3} is only a little less than the lower limit for tetrahedra. The usual coordination number for boron with oxygen is **3** (in the borate ion, $[BO_3]^{-3}$). **It** is **four,** however, in the 12-tungstoborate ion,[16] in which a stabilizing influence is exerted by the tungsten octahedra.

So far as I know, Al^{+3} has the coordination number 6 in all of its compounds with oxygen the structures of which have been determined. The coordination number 4 would also be expected for it, however; it is probable that it forms tetrahedra in some of its compounds, as, for example, γ-alumina, the cubic form of Al_2O_3, and the feldspars, in which there occurs replacement of Na^+ and Si^{+4} by Ca^{++} and Al^{+3}. This possibility is further discussed in Section 11.

Zr^{+4} has the coordination number 8 in zircon. The polyhedron of oxygen ions about it is, however, not a cube. It is on account of the ease with which these polyhedra are distorted that large cations, with coordination numbers greater than six, are not included in the field of application of the suggested principles. Octahedra and tetrahedra retain their approximate shapes even under the action of strong distorting forces, and, moreover, rules have been formulated governing the distortion that they do undergo (Section 9).

5. The Number of Polyhedra with a Common Corner. The Electrostatic Valence Principle.—The number of polyhedra with a common corner can be determined by the use of an extended conception of electrostatic valence. Let ze be the electric charge of a cation and ν its coordination number. Then the *strength of the electrostatic valence bond* going to each corner of the polyhedron of anions about it is defined as

$$s = \frac{z}{\nu} \tag{2}$$

Let $-\zeta e$ be the charge of the anion located at a corner shared among several polyhedra. We now postulate the following *electrostatic valence principle: I. In a stable coördination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner; that is, for each anion*

$$\zeta = \Sigma_i \frac{z_i}{\nu_i} = \Sigma_i s_i \tag{3}$$

In justification of this principle it may be pointed out that it places the anions with large negative charges in positions of large positive potentials; for the bond strength of a cation gives approximately its contribution to the total positive potential at the polyhedron corner (the factor $1/\nu$ accounting for the larger cation–anion distance and the greater number of adjacent anions in the case of cations with larger coordination number),

---

[16] Pauling, unpublished material.

and the application of the principle requires that the sum of these potentials be large in case the valence of the anion is large.

It is not to be anticipated that Equation 3 will be rigorously satisfied by all crystals. It should, however, be always satisfied approximately. As a matter of fact, almost all crystals which have been investigated conform to the principle. Equation 3 is necessarily true for all crystals the anions of which are crystallographically equivalent, such as corundum, Al_2O_3,[17] rutile, anatase, spinel, $MgAl_2O_4$, garnet, $Ca_3Al_2Si_3O_{12}$,[18] cryolithionite, $Na_3Li_3Al_2F_{12}$,[19] etc. It is also satisfied by topaz; each oxygen ion, common to one silicon and two aluminum ions, has $\Sigma s_i = 2$ (see Table II for a list of values of s), while each fluorine ion, attached to two aluminum ions only, has $\Sigma s_i = 1$. Similarly in beryl some oxygen ions are shared between two silicon ions, and some between one silicon, one beryllium and one aluminum ion; in each case $\Sigma s_i = 2$. In chondrodite, $H_2Mg_5Si_2O_{10}$, humite, $H_2Mg_7Si_3O_{14}$, and clinohumite, $H_2Mg_9Si_4O_{18}$, there are oxygen ions common to one silicon tetrahedron and three magnesium octahedra ($\Sigma s_i = 2$), and OH– groups common to three magnesium octahedra ($\Sigma s_i = 1$). This list of examples could be largely extended.

6. The Sharing of Edges and Faces.—The electrostatic valence principle indicates the number of polyhedra with a common corner but makes no prediction as to the number of corners common to two polyhedra; that is, whether they share one corner only, two corners defining an edge, or three or more corners defining a face. In rutile, brookite and anatase, for example, each oxygen ion is common to three titanium octahedra (and hence has $\Sigma s_i = 2$, satisfying Equation 3); but the number of edges shared by one octahedron with adjoining octahedra is two in rutile, three in brookite and four in anatase. In corundum on the other hand, each aluminum octahedron shares one face and three edges with other octahedra. The reason for this difference is contained in the following rule. **III.** *The presence of shared edges, and particularly of shared faces, in a coördinated structure decreases its stability; this effect is large for cations with large valence and small coördination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.*

This decrease in stability arises from the cation–cation Coulomb terms. The sharing of an edge between two regular tetrahedra brings the cations at their centers to a distance from each other only 0.58 times that obtaining in case the tetrahedra share a corner only; and the sharing of a face decreases this distance to 0.33 times its original value (Fig. 5). The corresponding positive Coulomb terms cause a large increase in the crystal energy and decrease in the stability of the structure, especially for highly

---

[17] Linus Pauling and S. B. Hendricks, THIS JOURNAL, 47, 781 (1926).

[18] G. Menzer, *Z. Krist.*, *63*, 157 (1926).

[19] G. Menzer, *ibid.*, 66, 457 (1927).

charged cations. The effect is not so large for regular octahedra, amounting to a decrease in the cation–cation distance to the fractional value 0.71 for a shared edge and 0.58 for a shared face.

These calculated decreases are valid only in case the change in structure is not compensated by deformation of the polyhedra. Some compensating deformation will always occur; the rules governing deformation (Section 9) show that it will be small in case the radius ratio approaches the lower limit of stability for the polyhedron, and will increase with the radius ratio.

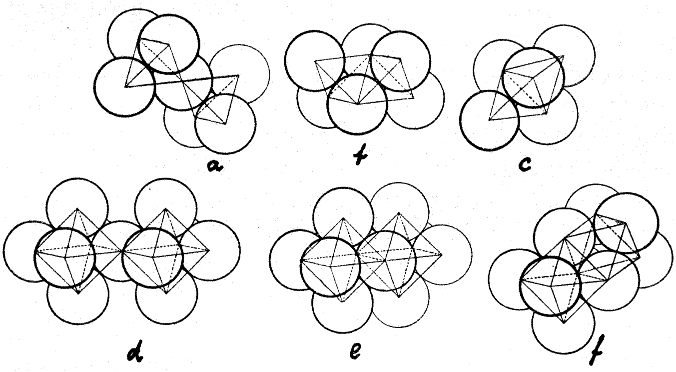


Fig. 5.—a, *b* and *c* show two tetrahedra of oxygen ions with a corner, an edge and a face in common; *d*, e and *f* show two octahedra of oxygen ions with a corner, an edge and a face in common.

In agreement with expectation, silicon tetrahedra tend to share only corners with other polyhedra when this is possible (as in topaz, $Al_2SiO_4F_2$, etc.), titanium octahedra share only corners and edges, while aluminum octahedra, when constrained by the stoichiometrical formula of the substance, will share faces in some cases, as in corundum, Al_2O_3. The effect of large radius ratio in diminishing the instability due to an increase in the number of shared edges is shown by the approximate equality in free energy of rutile, brookite and anatase, with two, three and four shared edges, respectively. As a matter of fact, the order of stability is just that of the number of shared edges, rutile being the most stable,[20] in agreement with expectation. Many other dioxides also crystallize with the rutile structure but no other is known with the brookite or anatase structure.

The effect of small valence and large coordination number is further shown by the observation that silicon tetrahedra, which share comers only with aluminum octahedra, share edges with magnesium octahedra (in olivine, chondrodite, humite, clinohumite) and with zirconium polyhedra with coordination number eight (in zircon).

7. **The Nature of Contiguous Polyhedra.**—*IV. In a crystal con-*

---

[20] C. Doelter, "Handbuch der Mineralchemie," Theodor Steinkopff, Dresden, 1918, Vol. III, Part 1, p. 15.

taining different cations those with large valence and small coordination number tend not to share polyhedron elements with each other. This rule follows directly from the fact that cations with high electric charges tend to be as far apart from each other as possible, in order to reduce their contribution to the Coulomb energy of the crystal.

The rule requires that in silicates the silicon tetrahedra share no elements with each other if the oxygen–silicon ratio is equal to or greater than four (topaz, zircon, olivine, orthosilicates in general). If stoichiometrically necessary, corners will be shared between silicon tetrahedra, but not edges or faces. In the various forms of silicon dioxide all four corners of each tetrahedron are shared with adjoining tetrahedra. In diorthosilicates the Si_2O_7 group is formed of two tetrahedra sharing a corner. The metasilicates should not contain groups of two tetrahedra with a common edge, but rather chains or rings, each tetrahedron sharing two corners (as in beryl, with a ring of six tetrahedra, stable because of the approximation of the tetrahedral angle to 120°). Other silicates are no doubt similar. It is of interest that the electrostatic valence principle requires that corners shared between two silicon tetrahedra be not shared also with other polyhedra; this is true for beryl.

8. The Rule of Parsimony.—V. *The number of essentially different kinds of constituents in a crystal tends to be small.* First, the electrostatic bonds satisfied by all chemically similar anions should be the same if possible (topaz, all oxygen ions common to two aluminum octahedra and one silicon tetrahedron, all fluorine ions common to two aluminum octahedra). This does not require the anions to be crystallographically equivalent (in topaz the oxygen ions are crystallographically of three kinds, in brookite of two kinds); crystallographic non-equivalence does not imply essential difference from the standpoint of the coordination theory. Often the preceding rules do not permit all anions to be alike, as, for example, in the case of silicates with an oxygen–silicon ratio greater than four, in which the four orthosilicate oxygens are necessarily different from the others. In these cases the number of different kinds of anions will, however, be small.

Second, the polyhedra circumscribed about all chemically identical cations should, if possible, be chemically similar, and similar in their contiguous environment, that is, in the nature of the sharing of corners, edges and faces with other polyhedra. For example, each aluminum octahedron in topaz has as corners four oxygen and two fluorine ions, and each shares two edges with other octahedra and four corners with silicon tetrahedra. The titanium octahedron in rutile shares two edges, in brookite three and in anatase four, but no structure is known in which these different octahedra occur together. The polyhedra which are similar in these respects may or may not be crystallographically equivalent, for they may differ in their remote environment. Thus the contiguously similar tetrahedra of silicon atoms about carbon atoms in carborundum are crystallographically of several kinds (five in carborundum I).

9. Distortion of the Polyhedra.—The above rules suffice to indicate the nature of the structure of a given crystal, so that a structure can be composed of regular polyhedra in accordance with them, and its space-group symmetry and approximate dimensions compared with those found by x-ray analysis. In this way a structure can be identified as giving approximately the correct atomic arrangement (as was done for brookite and for topaz); but the actual atomic arrangement may differ considerably from this "ideal" arrangement corresponding to regular polyhedra, as a resultant of distortion of the polyhedra. The investigation of the agreement between observed intensities of x-ray reflections and structure factors calculated for all atomic arrangements involving small displacements from the ideal arrangement would be extremely laborious. It is accordingly desirable to be able to predict with some accuracy the nature and the amount of the distortion to be expected for a given structure.

In not too complicated cases this can be done theoretically by finding the minimum in the crystal energy with respect to variations in the parameters determining the structure, with the use of a theoretical expression for the interionic repulsion potential. Such calculations have been carried out for rutile and anatase,[21] leading to the result that in each case the shared edges of the titanium octahedra are shortened to the length 2.50 Å., other edges being compensatorily lengthened. This distortion is actually found experimentally for these crystals. It was accordingly assumed to hold for brookite also, and the atomic arrangement derived in this way was shown to be in complete agreement with the observed intensities of x-ray reflection.

In general it is not possible to make such calculations on account of the excessive labor involved. It can be seen, however, that the cation–cation repulsion will shorten shared edges and the edges of shared faces, and reasonably confident application may be made of the following rule. Polyhedra of oxygen ions about trivalent and tetravalent cations are distorted in such a way as to shorten shared edges and the edges bounding shared faces to a length of about 2.50 Å. Edges bounding shared faces have been observed to be shortened to 2.50 Å. in corundum, Al_2O_3, and to 2.55 Å. in hematite, Fe_2O_3, in agreement with the foregoing rule.

It is furthermore to be anticipated that the cation–cation repulsion will operate in some cases to displace the cations from the centers of their coordinated polyhedra. This action will be large only in case the radius ratio approaches the lower limit for stability, so that the size of the polyhedron is partially determined by the characteristic anion–anion repulsive

---

[21] Linus Pauling, *Z. Krist.*, **67**, *377* **(1928).**

forces (the distribution of closely neighboring cations must, of course, be one-sided in addition). Hematite and corundum provide an example of this effect. In these crystals each octahedron shares a face with another octahedron. Now in an iron octahedron, with radius ratio about 0.48, the repulsive forces principally effective in determining the interionic distances are those between iron and oxygen ions. The Coulomb repulsion of the two iron ions accordingly can produce only a small displacement of these ions from the octahedron centers; the iron ions in hematite are observed to be 2.06 Å. from the oxygen ions defining the shared face and 1.99 Å. from the other oxygen ions. In an aluminum octahedron, on the other hand, with radius ratio 0.41, the characteristic repulsive forces between oxygen ions as well as those between oxygen and aluminum ions are operative; as a result of this "double repulsion"[12] the distance from the center of the octahedron to a corner is somewhat greater than the sum of the crystal radii of aluminum and oxygen. The aluminum ions are correspondingly mobile and the aluminum–aluminum Coulomb repulsion is to be expected to cause a large displacement in their positions. This is observed; the two aluminum-oxygen distances in corundum are 1.99 Å. and 1.85 Å.

The nature and approximate amount of the distortion to be expected in other cases can be similarly estimated; an example will be given in a later paper.[16]

10. The Close-Packing of Large Ions.—In piling together polyhedra in the attempt to predict a possible structure for a crystal with the aid of the principles described above, the recognition from the observed dimensions of the unit of structure that the atomic arrangement is probably based on a close-packed arrangement of the anions is often of very considerable assistance, for it indicates the probable orientation of the polyhedra, which can then be grouped together to form the completed structure. This was done in the determination of the structure of topaz and contributed considerably to the ease of solution of the problem. The approximation of the dimensions of the unit of structure of topaz to those of a close-packed structure does not, however, suffice to determine the positions of the anions, for there are two types of close-packing, simple hexagonal and double hexagonal,[22] which have these dimensions. This ambiguity

[22] An infinity of equally close-packed arrangements of spheres can be made from the close-packed layers A, with a sphere at $X = 0$, $Y = 0$ (X, Y and Z being hexagonal coördinates), B, with a sphere at $X = 1/3$, $Y = 2/3$, and C, with a sphere at $X = 2/3$, $Y = 1/3$. For simple hexagonal close-packing these layers are superposed in the order ABABAB..., for cubic close-packing in the order ABCABC... for double hexagonal close-packing in the order ABACABAC..., and so on, with ever-increasing complexity. In only the first two are the spheres crystallographically equivalent, and only these two have been generally recognized in the past; this restriction is, however, undesirable from the standpoint of the coordination theory.

was no serious obstacle in the prediction of the structure by the coordination method; the octahedra and tetrahedra were suitably piled together and the resultant arrangement of oxygen and fluorine ions was found to be double hexagonal close-packing.

Hrookite is also based upon a double hexagonal close-packed arrangement of the oxygen ions. The dimensions of the unit of structure differ so much on account of distortion from those for the ideal arrangement, however, that the existence of close-packing was recognized only after the structure had been determined.

It may be pointed out that in some structures easily derivable with the coördination theory, such as the rutile structure, the anion arrangement approximates no type of close-packing whatever.

11. Applications of the Theory.—As an illustration of the application of the foregoing principles some predictions may be made regarding the structure of cyanite, andalusite and sillimanite, the three forms of Al_2SiO_5. From the rule of parsimony we expect all aluminum octahedra to be similar and all silicon tetrahedra to be similar. Let the number of octahedra one corner of which is formed by the i^{th} oxygen ion be α_i; then the stoichiometrical oxygen–aluminum ratio, 5:2, requires that

$$\sum_i \frac{1}{\alpha_i} = \frac{5}{2} \tag{4}$$

in which the sum is taken over the six oxygen ions forming one octahedron. Four out of five oxygen ions, in accordance with Rule IV, will be distinguished through being attached to silicon ions; this fact is expressed by the equation

$$\sum_i{}' \frac{1}{\alpha_i} = 2 \tag{5}$$

in which the prime signifies that the sum is to be taken over these oxygen ions only. Let us now assume that the oxygen ions are of only two kinds with respect to their values of a, those attached to silicon ions, n_1 in number, forming one class, and those not attached to silicon ions, n_2 in number, forming the other class. Equations 4 and 5 then become

$$\left.\begin{aligned} \frac{n_1}{\alpha_1} + \frac{n_2}{\alpha_2} &= 5/2 \\ \frac{n_1}{\alpha_1} &= 2 \end{aligned}\right\} \text{ with } n_1 + n_2 = 6 \tag{6}$$

The only solution of these equations involving integers is $n_1 = 4$, $\alpha_1 = 2$, $n_2 = 2$, $\alpha_2 = 4$. Thus about each aluminum ion there will be four oxygen ions common to two aluminum octahedra and one silicon tetrahedron, and two oxygen ions common to four octahedra.[23] For both kinds of oxy-

---

[23] It is possible that the aluminum octahedra may be of more than one kind. In this case average values of the sums would have to be used in Equations 4 and 5, and the equations would no longer possess a single solution.

gen ions $\Sigma s_i = 2$, so that the principle of electrostatic valence, which was not used in the derivation of Equation 6, is satisfied.

This result, while limiting considerably the number of possible structures for these crystals, by no means determines their structures. Further information is provided by Rule III, from which it is to be expected that the silicon tetrahedra share only corners with aluminum octahedra, and the octahedra share only corners and edges (and possibly one face) with each other.

These predictions are not incompatible with Professor Bragg's assignment of a cubic close-packed arrangement of oxygen ions to cyanite.[7a] They are, however, in pronounced disagreement with the complete atomic arrangement proposed by Taylor and Jackson,[24] whose suggested structure conflicts with most of our principles. Their structure is far from parsimonious, with four essentially different kinds of octahedra and two of tetrahedra. Each silicon tetrahedron shares a face with an octahedron, contrary to Rule III. The electrostatic valence principle is not even approximately satisfied; one oxygen ion, common to four aluminum octahedra and one silicon tetrahedron, has $\Sigma s_i = 3$, while another, common to two octahedra only, has $\Sigma s_i = 1$. For these reasons the atomic arrangement seems highly improbable.

The coordination theory and the principles governing coördinated structures provide the foundation for an interpretation of the structure of the complex silicates and other complex ionic crystals which may ultimately lead to the understanding of the nature and the explanation of the properties of these interesting substances. This will be achieved completely only after the investigation of the structures of many crystals with x-rays. To illustrate the clarification introduced by the new conception the following by no means exhaustive examples are discussed.

Let us consider first the silicates of divalent cations with coordination Number 6, and hence with electrostatic bond strength $s = {}^1/_3$. An oxygen ion forming one comer of a silicon tetrahedron would have $\Sigma s_i = 2$ if it also formed a corner of three R^{++} octahedra; if it were not attached to a silicon ion, it would have to form a corner of six R^{++}octahedra to satisfy the electrostatic valence principle. But six octahedra can share a corner only by combining in the way given by the sodium chloride structure, and this arrangement, involving the sharing of many edges, is expected not to be stable as a part of the structure of a complex silicate.[25] Accordingly, we conclude that no oxygen ions not attached to silicon occur in these silicates; that is, the oxygen–silicon ratio cannot be greater than

---

[24] W. H. Taylor and W. W. Jackson, *Proc.* Roy. *Soc. London,* **119A, 132** (1928).

[25] The instability of the sodium chloride structure for oxides is shown by the heat of the reactions $CaO + H_2O = Ca(OH)_2 +$ 15,500 cal. and $MgO + H_2O = Mg(OH)_2 +$ 9000 cal.

4:1. The silicates which will occur are orthosilicates, $R^{++}{}_2SiO_4$, metasilicates, $R^{++}SiO_3$, etc. This is verified by observation; no basic silicates of such cations are known, although many normal silicates such as forsterite Mg_2SiO_4, etc., exist.

A univalent anion (F^-, $OH-$) may be shared among three R^{++}octahedra alone, so that compounds may occur in which these anions are present in addition to the SiO_4 groups. Such compounds are known: $Mg_3SiO_4(F, OH)_2$, prolectite, $Mg_5(SiO_4)_2(F, OH)_2$, chondrodite, etc.

Compounds of simple structure according to the coordination theory are those in which the number of essentially different kinds of anions is small. In a simple orthosilicate containing aluminum and a divalent cation each oxygen ion would form the corner of a silicon tetrahedron ($s = 1$), an aluminum octahedron ($s = {}^1/_2$), and one or two R^{++} polyhedra (one tetrahedron or two polyhedra with $v = 8$). The composition of the substance would then be given by the formula $R^{++}{}_3Al_2Si_3O_{12}$. Similarly, in simple metasilicates there would occur such oxygen ions in addition to those common to two silicon tetrahedra; the corresponding formula is $R^{++}{}_3Al_2Si_6O_{18}$. This result is in striking agreement with observation. The most important double orthosilicates of divalent and trivalent metals are the garnets: $Ca_3Al_2Si_3O_{12}$, grossular, $Ca_3Cr_2Si_3O_{12}$, uvarovite, $Ca_3Fe_2Si_3O_{12}$, topazolite, etc., and the only double metasilicate is beryl, $Be_3Al_2Si_6O_{18}$.

The radius ratio of potassium ion and oxygen ion is 0.76, so that the coördination number to be expected for potassium ion in silicates is 8, the corresponding electrostatic bond strength being ${}^1/_8$. In potassium aluminum silicates containing aluminum octahedra the electrostatic valence principle would require at least four potassium polyhedra to have a common corner together with a silicon tetrahedron and an aluminum octahedron; this is not spatially possible. It is accordingly highly probable that in these compounds, the structure of none of which has yet been satisfactorily investigated with x-rays, the aluminum ions have a coordination number of 4. There could then occur oxygen ions with $\Sigma s_i = 2$ common to a silicon tetrahedron, an aluminum tetrahedron and two potassium polyhedra. The potassium–aluminum ratio would then be 1:1. In a large number of silicates, in particular the important feldspars, this ratio is observed: $KAlSiO_4$, phakelite, $KAlSi_2O_6$, leucite, $KAlSi_3O_8$, potassium feldspar (microcline, orthoclase), $(K, Na)_8Al_8Si_9O_{34}$, nepheline, etc. In other silicates containing more than this amount of aluminum, such as muscovite, $H_2KAl_3Si_3O_{12}$, etc., it is probable that the excess aluminum ions usually have the coordination Number 6.

Other alkali ions (except lithium) also probably have the coordination Number 8 as a rule, and should similarly have a tendency to a 1:1 ratio with aluminum; this is shown in $NaAlSi_3O_8$, albite, $H_2Na_2Al_2Si_3O_{12}$, natrolite, $H_2Cs_4Al_4Si_9O_{27}$, pollucite, etc.

In spodumene, $LiAlSi_2O_6$ and petalite, $LiAlSi_4O_{10}$, it is possible that oxygen ions (with $\Sigma s_i = 2$) are common to a silicon tetrahedron, an aluminum tetrahedron and a lithium tetrahedron (the radius ratio for lithium ion is 0.33).

No aluminum silicates of alkali metals are known in which the Al^{+3}:R^{+1} ratio is less than 1:1.

Summary

A set of principles governing the structure of complex ionic crystals, based upon the assumption of a coordinated arrangement of anions about each cation at the corners of an approximately regular polyhedron, is formulated with the aid of considerations based upon the crystal energy. Included in the set is a new electrostatic principle which is of wide application and considerable power.

It is shown that the known structures of many complex crystals, in particular the complex silicates, satisfy the requirements of these principles.

As an illustration of the application of the principles in the prediction of structures with the coordination theory, some properties of the structures of the three forms of Al_2SiO_5, cyanite, andalusite and sillimanite, are predicted.

It is further shown that the theory requires that no stable basic silicates of divalent metals exist, and that in aluminum silicates of alkali metals there should be at least one aluminum ion for every alkali ion.

The structures of aluminum silicates of divalent metals which are simplest from the coordination standpoint are shown to correspond to the formulas $R_3^{++}Al_2Si_3O_{12}$ and $R_3^{++}Al_2Si_6O_{18}$, which include the most important minerals of this class, the garnets and beryl.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

SOLUBILITY IN THE GASEOUS PHASE, ESPECIALLY IN THE SYSTEM: $NH_3(l)$-$NH_3(g)$, $H_2(g)$, $N_2(g)$

BY H. L. CUPPLES

RECEIVED SEPTEMBER 7, 1928 PUBLISHED APRIL 5, 1929

A number of investigators have found that a solubility effect may be shown within a gaseous phase, especially under circumstances in which the density of the gaseous phase is relatively high. Pollitzer and Strebel[1] were perhaps the first to mention this phenomenon.

The two-phase system $NH_3(l)$-$NH_3(g)$, $H_2(g)$, $N_2(g)$ in which the H_2 and N_2 were maintained at the constant mole ratio of $3H_2$:N_2 has been experimentally investigated by Larson and Black.[2] Concentrations

---

[1] Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 785 (1924).

[2] Larson and Black, THIS JOURNAL, 47, 1015 (1925).

of ammonia in the gas phase were found to be as much as six times the concentrations calculated with the aid of the perfect gas laws, **and** an application of the Poynting equation[3] for increase of vapor pressure with total pressure did not yield satisfactory results. These authors suggest that the observed concentrations are possibly due to a positive solubility effect of the gaseous phase for ammonia vapor.

Lurie and Gillespie[4] have recently studied a similar system in which they measured the composition of mixtures of nitrogen and ammonia in equilibrium with a mixture of barium chloride and barium chloride octa-ammine, their experiments extending up to total pressures of approximately 60 atmospheres at 45°. At this temperature and within the pressure range studied it was found that the equilibrium concentrations of ammonia exhibited a considerable solubility effect when compared with values calculated with the assumption of Gibbs' rule of additive pressures. An applicaiion of the equation of state for mixtures of Keyes and Burks, however, yielded satisfactory agreement with the experimentally determined concentrations.

Considering the available data for a number of cases of gaseous solutions (including the NH_3–H_2–N_2 system), Randall and Sosnick[5] have presented *a* series of curves of "activity coefficients" which enable rough quantitative predictions of values in other mixtures and at other temperatures.

A Concept of "Zero Solubility."—In order that we may further examine the nature of phenomena similar to those mentioned above, it will be necessary first to define what we mean by "solubility" in systems of this kind. For this purpose let us consider a closed system containing only a gaseous component, A. Let us next imagine this system to be partially filled with a non-volatile liquid component, B, allowing none of Component A to escape from the system. It is apparent that, when equilibrium is attained, Component A will be uniformly distributed throughout the liquid phase and uniformly distributed throughout the gaseous phase, but in general its distribution will not be uniform throughout the system as a whole. With a certain choice of components, Component A might be found to be almost entirely in the liquid phase, its density in the gaseous phase being much less than its original density before the introduction of the liquid phase. This might be expressed by stating that the gas is very soluble in the liquid. With another choice of components, Component A might remain largely in the gaseous phase, its density accordingly being greater than before the introduction of the liquid. In this case the gas might be said to be comparatively insoluble in the liquid.

---

[3] Poynting, **Phil.** *Mag.*, **[4] 12, 32 (1881).**

[4] Lurie and Gillespie, THIS JOURNAL, 49, **1146 (1927).**

[5] Randall and Sosnick, *ibid.*, 50, **967** (1928).

The unique case is that in which Component A remains uniformly distributed throughout the entire system, its density in each phase being identical with its original density before introduction of the liquid. As the spatial distribution of Component A is in this case entirely unaffected by the presence of Component B, it follows that the activity of Component A at each point throughout the system is dependent only on its volume concentration and temperature. It seems quite logical to consider this as a case of "zero solubility," and from this point of view we may define a "solubility effect" as being a change in the activity of one component which is due to the presence of other components.

Application to the System **NH_3(l)-NH_3(g), H_2(g), N_2(g).**—Let us first consider a simple closed system containing liquid ammonia in equilibrium with ammonia gas at constant temperature. Under these conditions the pressure exerted by the ammonia vapor is the normal vapor pressure of ammonia at the temperature considered. Next let us imagine the liquid phase to be separated from the gaseous phase by a piston permeable to ammonia vapor but impermeable to ammonia liquid; by means of this piston let us exert a definite pressure upon the liquid phase, thus increasing the activity of ammonia in this phase. If equilibrium conditions are maintained, it is evident that the activity of ammonia in the gaseous phase will correspondingly increase; this increase in activity is developed by an increase in the density of ammonin in the gas phase. The net result is that increase of pressure on the liquid ammonia phase causes an increase in the density of ammonia in the gas phase; this phenomenon is often referred to as the Poynting effect. It is obvious that no solubility effects are involved in the Poynting effect, as the gas phase is assumed to contain no constituent other than ammonia.

We may, however, employ a different device for exerting pressure upon the liquid ammonia phase. In the absence of the semi-permeable membrane which has previously been assumed to exert this pressure, let us pump into the system an "inert" gas which is substantially insoluble in the liquid phase. By this means we may exert the same pressure on the liquid ammonia as was previously exerted through the assumed semi-permeable membrane. The significant difference between conditions in the two assumed cases is that in this second case the gas phase contains a high concentration of the "inert" gas. The question at once arises as to whether or not this "inert" gas has a solubility effect. It seems logical to consider that no solubility effect is exhibited if the volume concentration of ammonia in the gaseous phase is identical with what it would be were the same pressure applied to the liquid phase through the medium of a semi-permeable piston. This is in conformity with the definition of solubility effect which we have developed above, namely, that a solubility effect is a change in the activity of the solute due to the presence of the solvent; in this case the solvent is the "inert" gas by means of which we exert an increased pressure upon the liquid ammonia, while the solute is the ammonia in the gas phase.

We may now proceed to examine this system in greater detail, in accordance with our present conception of a solubility effect.

Activity of Ammonia in the Liquid Phase.—The activities of liquid ammonia at pressures greater than its normal vapor pressure, relative to its activity a' at the same temperature and under the pressure of its saturated vapor, have been calculated by applying the equation[6]

---

[6] See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. *225.*

$$RT \ln a/a' = \int_{P'}^{P} V dP \qquad (1)$$

This calculation has been made in a manner entirely similar to that used by Randall and Sosnick,[5] except that approximate corrections have been made for the decrease in volume of the liquid ammonia at pressures greater than the vapor pressure, and for the solubility of the $3H_2:N_2$ mixture in the liquid ammonia phase. For this purpose a rough value of 5×10^{-5} was used for the compressibility factor for liquid ammonia, and the solubilities of hydrogen and nitrogen in the liquid phase have been estimated by graphical interpolation and extrapolation of the data of Larson and Black,[7] who worked in this instance at pressures up to 150 atmospheres. The activity values as given by Randall and Sosnick would probably have been used in these calculations had they been available at the time this material was in course of preparation.

Activity of Ammonia in the Gaseous Phase.—The calculation of the concentration of ammonia in the gas phase from its activity presents difficulty. In the absence of experimental information Lewis and Randall[8] considered all gaseous solutions to be nearly perfect solutions, and assumed the fugacity of each constitutent to be proportional to the mole fraction of that constituent, at every temperature and at every pressure. More recent experimental data have shown that gaseous mixtures at higher pressures may present the same kinds of deviations as liquid mixtures, although the deviations are not, in general, so large.[5,9]

Keyes[10] has employed his equation of state for similar calculations with gaseous mixtures, assuming a simple additive rule for combining the constants of the individual gases to obtain the constants for the mixture.

For our present purpose we shall make the very simple assumption that the activity of ammonia vapor is dependent only on its volume concentration and temperature, and is entirely independent of the other gases which may be present. This is equivalent, according to the definition which we have adopted above, to assuming that there is no solubility effect toward ammonia vapor in the gas phase, and agreement of calculated with observed results will be a strong indication of the relative unimportance of such an effect.

Because of its convenient form for the direct evaluation of certain desired integrals, the P-V-T relationships of ammonia vapor will be expressed by means of the Bureau of Standards equation.[11] While it is known that this equation well reproduces the experimental data, its

---

[7] Larson and Black, *Ind. Eng. Chem.*, 17,715 (1925).

[8] Ref. 6, p. 225.

[9] Gibson and Sosnick, THIS JOURNAL, 49,2172–2179 (1927).

[10] Keyes, *ibid.*, 49, 1393 (1927).

[11] U. S. Bureau of Standards "Scientific Paper No. 501," 1925.

accuracy becomes increasingly uncertain as it is extrapolated to pressures which are increasingly greater than the normal vapor pressure of liquid ammonia at a particular temperature. Randall and Sosnick[5] have clearly shown how certain equations of state may lead to erroneous values of fugacity when they are too far extrapolated. It is easy to show that similar limitations apply to the Bureau of Standards equation of state, and for this reason the present calculations have not been extended beyond total pressures of 600 atmospheres.

Method of Calculation

The activities of liquid ammonia in the presence of compressed $3H_2:N_2$ mixture at various pressures and temperatures, calculated as previously described, are shown in Table I, Col. 3. These activities are relative to the activity of $NH_3(l)$ at the same temperature and under the saturation pressure of its own vapor. Under equilibrium conditions the activities in the liquid and gas phases are, of course, necessarily equal, when referred to the same standard state.

At a given temperature and total pressure it is next required to determine the pressure of ammonia vapor at which its activity will equal the activity of ammonia in the liquid phase. For this purpose Equation 1 has again been utilized, the integration being carried out by substituting for V its value in terms of P (at constant temperature), as given by the Bureau of Standards equation of state. At a given temperature this integral has been evaluated for a number of different values of P and a curve constructed in which a/a' has been plotted as ordinate against P as abscissa. From this plot it is then possible to read directly the value of P at which ammonia vapor has the same activity as its calculated value in the liquid phase. These values of P are given in Table I, Col. 4. Substitution of these values of P directly in the equation of state for ammonia vapor gives the corresponding values for the specific volumes of ammonia vapor. Multiplication by 17.03 gives the molal volumes as shown in Table I, Col. 5.

Let us now consider a volume of the compressed gaseous mixture in equilibrium with liquid ammonia, equal in cc. to RT, where RT is expressed in cc.-atm. At any given temperature and value of the molal volume of ammonia, RT/Molal Volume will represent the number of moles of ammonia contained in this volume. These values are given in Table I, Col. 6.

The number of moles of the "inert" gas ($3H_2:N_2$) which are present in this same volume will be estimated by an application of the principle of additive pressures. Consider a volume of $3H_2:N_2$ mixture in equilibrium with the mixture containing ammonia, through a membrane permeable to hydrogen and to nitrogen but impermeable to ammonia. We

TABLE I

OBSERVED AND CALCULATED DATA

Total press., atmos.	Temp., °C.	Activ. of NH_3 (l)	Press. of NH_3 (g)	Molal vol. NH_3 (g)	$\frac{RT}{\text{Molal vol.}}$	Moles of $3H_2:N_2$	Mole % of NH3 Calcd.	Mole % of NH3 From data of Larson and Black
50	−40	1.064	0.755	24762	0.772	48.0	1.59	
	−20	1.062	1.991	9800	2.12	46.8	4.34	5.70
	−10	1.060	3.05	6681	3.23	45.9	6.58	7.35
	0	1.057	4.50	4625	4.85	44.5	9.82	10.0
	10	1.057	6.46	3268	7.11	42.6	14.3	13.9
	20	1.056	9.00	2372	10.13	40.2	20.1	20.4
100	−40	1.135	0.808	23096	0.828	93.8	0.88	
	−20	1.126	2.122	9332	2.22	92.6	2.34	3.25
	−10	1.123	3.23	6284	3.43	91.8	3.60	4.35
	0	1.120	4.82	4280	5.23	90.5	5.47	5.80
	10	1.116	6.85	3062	7.58	88.5	7.90	8.00
	20	1.112	9.45	2241	10.73	86.2	11.07	11.10
200	−40	1.287	0.918	20254	0.944	176.0	0.53	..
	−20	1.264	2.42	8135	2.55	175.1	1.44	..
	−10	1.260	3.65	5509	3.91	174.7	2.20	..
	0	1.250	5.40	3790	5.91	173.5	3.30	..
	10	1.244	7.72	2670	8.70	172.1	4.82	..
	20	1.240	10.70	1936	12.42	169.8	6.83	..
300	−40	1.458	1.040	17803	1.074	246.3	0.43	
	−20	1.428	2.74	7120	2.92	246.4	1.17	1.50
	−10	1.412	4.13	4814	4.48	246.0	1.79	2.20
	0	1.400	6.12	3280	6.83	245.0	2.71	3.25
	10	1.390	8.71	2321	10.00	244.3	3.93	4.60
	20	1.370	12.00	1685	14.27	242.7	5.56	6.45
400	−40	1.649	1.180	15622	1.224	305.5	0.40	..
	−20	1.605	3.11	6210	3.34	307.0	1.08	..
	−10	1.583	4.68	4189	5.14	307.7	1.64	..
	0	1.565	6.91	2855	7.85	307.7	2.49	..
	10	1.549	9.87	1998	11.62	308.0	3.64	..
	20	1.536	13.90	1398	17.20	307.0	5.31	..
600	−40	2.113	1.530	11924	1.603	399.0	0.40	
	−20	2.023	3.95	4775	4.35	405.0	1.06	1.20
	−10	1.983	6.06	3118	6.91	407.0	1.67	1.70
	0	1.950	8.96	2092	10.71	409.0	2.55	2.40
	10	1.925	12.80	1434	16.19	411.0	3.79	3.50
	20	1.900	18.65	910	26.41	411.0	6.04	5.05

shall assume the density of the $3H_2:N_2$ mixture to be the same on both sides of the membrane, and the $3H_2:N_2$ mixture in both cases to exert a pressure equal to $(P-p)$, where P is the total pressure exerted by the mixture containing ammonia vapor and p is the pressure exerted by the ammonia vapor itself, as given in Table I, Col. 4. The number of moles of $3H_2:N_2$ mixture in the volume RT will accordingly equal the pressure $(P-p)$, in atmospheres, divided by a compressibility factor, F, where F is equal to the P V product for one mole of $3H_2:N_2$ mixture, at the temperature and pressure under consideration, divided by the value of RT at that temperature. Values for F have been estimated by graphical interpolation and extrapolation of the data of Bartlett, Cupples and Tremearne,[12] and the values thus calculated for the number of moles of $3H_2{:}N_2$ present in the volume RT are given in Table I, Col. 7.

The mole fractions of ammonia in the gaseous mixtures may be obtained by dividing the values given in Col. 6 for the number of moles of ammonia in the volume RT, by the sum of the values in Cols. 6 and 7. These values, in mole per cent., are shown in Col. 8. In Col. 9 are shown the corresponding values which have been graphically interpolated from the experimental data of Larson and Black.

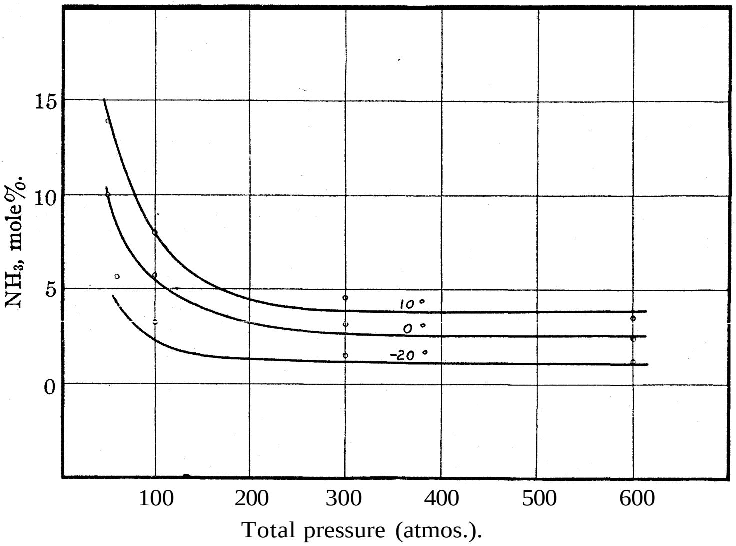


Fig. 1.—Mole percentage of ammonia in $3H_2{:}N_2$ mixture in equilibrium with liquid ammonia. Curves show calculated values; circles show experimental values.

Discussion

Considering the nature of the calculations and the assumptions which are necessarily involved, the calculated values may be said to be in good agreement with the experimental data. Within the pressure range covered by the calculations (600 atmospheres' total pressure), there seems to be no consistent deviation of substantial magnitude, such as would be shown if the gaseous phase had a significant solubility effect for ammonia vapor. Although there is a considerable deviation at the lower temperatures measured by Larson and Black, as illustrated in Fig. **1,** it should be noted that this deviation *does not increase with increasing*

---

[12] Bartlett, Cupples and Tremearne, THIS JOURNAL, 50, 1275 (1928)

pressure, as would be expected if it were due to a solubility effect of the compressed gaseous mixture.

A point of interest which appears from these calculations is the fact that comparatively little reduction in the mole per cent. of ammonia in the gas mixture is to be expected on increasing the total pressure beyond 600 atmospheres. At 0° an increase of pressure from 600 to 1000 atmospheres will decrease the volume of the gas mixture to about 75% of its initial value, simultaneously increasing the activity of $NH_3(l)$ to 152% of its initial value. It is quite possible that at some pressure a minimum value is attained, beyond which the mole per cent. of ammonia in the gas phase increases with increasing pressure. A few of the calculated values do, in fact, indicate a somewhat higher molal concentration of ammonia at 600 atmospheres' total pressure than at 400 atmospheres' total pressure, but at these high pressures this may possibly be due, at least in part, to errors incident to the extrapolation of the equation of state for ammonia vapor.

Summary and Conclusions

A concept of solubility is presented which seems to be especially applicable to systems involving one or more gaseous components. According to this concept, a solubility effect is defined as being a change in the activity of one component which is due to the presence of other components.

A method is outlined by which the two-phase system $NH_3(l)$–$NH_3(g)$, $H_2(g)$, $N_2(g)$ has been examined for the presence of such a solubility effect. It is concluded that, within the fairly large error of calculation, there is no indication of a solubility effect of the gas phase for ammonia vapor.

An analogous treatment can be applied to other similar systems for which the required data are available. It is to be expected that the conclusions which may be reached will vary in each individual case.

WASHINGTON, D. C.

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

THE OXIDATION OF IODIDE ION BY PERSULFATE ION. I. THE EFFECT OF TRI-IODIDE ION FORMATION ON THE REACTION VELOCITY[1]

BY ERIC JETTE AND CECIL V. KING

RECEIVED SEPTEMBER 15, 1928 PUBLISHED APRIL 5, 1929

A. Introduction

Thermal and photochemical reactions in which iodine is liberated from iodides by oxidizing agents have been the subject of numerous investigations, in nearly all of which the effect of the equilibrium $I_2 + I^- \quad I_3^-$ has been considered, although not always in an adequate manner. As a general conclusion from such investigations it may be said that one cannot predict with assurance what effect the presence of tri-iodide ion will have on any particular reaction since it depends largely upon the specific properties of the system. In connection with another problem the present writers were forced to investigate in some detail one of these reactions, namely, that between persulfate and iodide ions, a reaction which has been used by Bronsted[2] as a confirmation of his theory of reaction velocity.

The first to work with this reaction was Price,[3] who observed in one of his many experiments that adding iodine to the initial mixture decreased the velocity of the reaction and noted that the probable cause was the formation of tri-iodide ion. The single experiment which Price performed with iodine present in the initial mixture does not supply sufficient information for detailed study of the tri-iodide ion effect. Recently Kiss and his co-workers[4] have investigated the reaction and found (*cf.* Table IV of ref. 4c) that the presence of iodine in the initial mixture decreased the reaction velocity, but when the concentration of iodide ion was corrected for the amount of tri-iodide present, the velocity constant was the same as when no iodine was present at the beginning of the experiment. On this basis they concluded that the tri-iodide ion does not react with the persulfate ion. The work of Kiss, Bruckner and Zombory is seriously marred (1) by errors or gross misprints in the equations for the reaction velocity and for the concentration of tri-iodide ion, (2) by so incomplete a statement as to the meaning of their quantitative values and symbols that after

---

[1] Presented at the Swampscott meeting of the American Chemical Society, September 12, 1928.

[2] Bronsted, *Z. physik. Chem.*, 102, 169 (1922).

[3] Price, *ibid.*, 27, 474 (1898).

[4] (a) Kiss and Bruckner, *Z. physik. Chem.*, *128*, *71* (1927); (b) Kiss, *ibid.*, 134, 26 (1928); (c) Kiss and Zombory, Rec. *trav. chim.*, *46*, 225 (1927); (d) Kiss and Bossányi, *ibid.*, 47, 619 (1928).

considerable effort the present writers were unable to use the experimental results quoted in the correct equations or to calculate the constants given in the original communication and **(3)** by the presence of an unknown impurity in the persulfate used for nearly all their experiments, resulting in velocity constants approximately 15% too high; this fact was found and noted by the original experimenters. While all the calculations contained in each one of the papers quoted are presumably made on the same basis, the conclusions regarding the neutral salt effects, agreement with the Bronsted theory and the mechanism of the catalytic effects of iron and copper ions must remain in considerable doubt until the quantitative results are recalculated on a correct basis. More detailed criticisms will be given at various points in the present paper.

B. Materials and Methods

All the salts used in this investigation were "C. P." materials, which were recrystallized at least once from distilled water before using. The potassium persulfate (Baker's "Analyzed") was recrystallized between 50 and 0° and dried over sulfuric acid in a vacuum desiccator. The iodine was a "C. P." grade which was resublimed once with addition of potassium iodide and the product then sublimed once more. The particular purpose of purifying these salts and iodine was for the removal of traces of ferric salts which might have been present, especially in the persulfate, since ferric ion has a very pronounced catalytic effect on the reaction. No observable color was obtained on adding ammonium thiocyanate to any of these salts. Two different lots of each of the three principal substances, potassium iodide, potassium persulfate and iodine were prepared during the course of the investigation. Reaction velocity curves obtained with the first and second lots agreed within experimental error.

The water used in making the solutions was ordinary laboratory distilled water redistilled from potassium permanganate acidified with sulfuric acid and condensed in a block tin condenser, the first portions being rejected.

Most of the solutions, including the potassium persulfate and potassium iodide solutions, were made up by weighing the proper amount of dry salt, dissolving and making up to volume in standardized flasks. The iodine in solutions containing it at the start of the reaction was titrated before use by the method used later in determining the reaction velocity curve. The sodium thiosulfate solution used for the iodine titrations was standardized at frequent intervals against the iodine liberated from potassium iodide solutions by standard potassium permanganate solution, using freshly prepared starch solution as indicator. The concentration of the permanganate solution was determined by means of pure sodium oxalate.

Preliminary experiments carried out in glass-stoppered bottles gave continuously decreasing values for the bimolecular "constant," a result which might have been due to loss of iodine from the solution. In order to eliminate this possibility all the experiments reported in the present article were conducted in sealed pyrex bulbs each containing 50 cc. of the reaction mixture measured from standardized pipets. In most cases the bulbs were of 100-cc. capacity.

Equal volumes of the two solutions (usually measured from the same flask) were mixed as rapidly as possible, pipetted quickly into the prepared bulbs and sealed. They were then placed in a large thermostat at a temperature of 25.00 ±0.01°. After the reaction had proceeded for a given time, the tip of the bulb was removed and the titration of the iodine by means of a standardized sodium thiosulfate solution (approximately 0.01 molar) completed in the shortest possible time, the entire titration taking place without transferring the solution from the bulbs. Since the openings of the bulbs were quite small, and the titrating solution was made to flow over the inner surface of the bulb, and especially since the iodine in the solution was reduced to a very low concentration in less than one-half minute after opening, practically no loss of iodine occurred. Whenever the speed of the reaction was not too great, an excess of thiosulfate was added and the first titration checked by a back titration with a standard iodine (in potassium iodide) solution. In spite of these precautions, however, the velocity constants still decreased as the reaction proceeded, showing that the effect must be inherent in the reaction, as it has been considered by other investigators from results obtained by methods differing somewhat in details.

In some of the experiments the initial reaction mixture was saturated or nearly so with iodine. In these cases the individual solutions containing potassium persulfate and potassium iodide were saturated separately with iodine and 25-cc. samples of the solutions were titrated immediately to obtain the initial amount of iodine present. Into each reaction bulb 25 cc. of each of the two solutions were pipetted from standardized pipets. The solubility of iodine in the final mixture was unknown but this was not particularly important for the present purpose; if the final solution was not quite saturated just after mixing, it became so very soon due to the iodine formed by the reaction. The minimum time required for these titrations was two minutes, the maximum about five minutes, which accounts for the slight irregularities in the results with saturated iodine solutions. In these experiments also the entire titration was performed in the reaction bulb.

C. Theory and Results of Experiments with Initial Solutions Containing Only Potassium Persulfate and Potassium Iodide

The reaction between $S_2O_8^{-}$ and I^- ions has usually been considered a bimolecular reaction, although the stoichiometric equation for the potassium salts is

$$2KI + K_2S_2O_8 \longrightarrow 2K_2SO_4 + I_2 \tag{1}$$

The main reason for so considering it is the fact that the velocity constants as calculated from experimental results[5] by means of the ordinary bimolecular equation

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}C_{I^-} \tag{2}$$

or one of its integrated forms, showed less variation than if the equations for unimolecular or trimolecular reactions were used. The values of k obtained always decreased as the reaction progressed, the decrease being accounted for by the formation of the tri-iodide ion.

Bronsted considers the reaction to take place in two steps, the first of which is the formation of a critical complex, namely:

$$S_2O_8^{--} + I^- \longrightarrow (S_2O_8I)^{---} \tag{3}$$

$$(S_2O_8I)^{---} + I^- \longrightarrow 2SO_4^{--} + I_2 \tag{4}$$

On the basis of these reactions and his theory of reaction velocity, Brönsted writes the velocity equation

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}C_{I^-}\frac{f_{S_2O_8^{--}}f_{I^-}}{f_{(S_2O_8I)^{---}}} = kC_{S_2O_8^{--}}C_{I^-}F \tag{5}$$

---

[5] Cf. Price, ref. **3,** p. 477.

in which f represents the activity coefficients of the ions indicated and F is called the "kinetic activity factor." Since all the ions in Equation 3 have the same sign, the salt effect is positive and with increasing ionic strength the value of k should increase. If the initial concentration of $K_2S_2O_8$ is a moles per liter and that of KI is $2a$, then the initial ionic strength[5] of the solution is $5a$ while after the reaction has gone to completion it is $6a$ so that the value of k should increase in each experiment. A large amount of data is at hand to show that if the ionic strength of the solution is increased by the addition of ionogens which do not take part in the reaction, the reaction velocity increases. This confirmation of Brönsted's theory has already been pointed out by Kiss and Zombory and Kiss and Bruckner as well as by Bronsted.

Three possible assumptions which may be made in discussing the effect of the tri-iodide ion formation on the speed of reaction are as follows. (1) The tri-iodide ion does not react with the persulfate ion. (2) The tri-iodide ion reacts at the same rate as the iodide ion. (3) The tri-iodide ion reacts but at a rate different from that of the iodide ion. The first assumption was made by Kiss and Zombory and Kiss and Bossányi and will be shown to be incorrect. The second is improbable from the start since the reaction should then proceed just as if no tri-iodide ion was formed and it would be necessary to invoke the aid of unknown inhibitors to account for the actual behavior of the velocity curve. The third assumption will be shown to be correct in the present article. Before proceeding to this point, however, it will be pertinent to demonstrate that correcting the momentary iodide-ion concentration for the presence of tri-iodide ion is quite inadequate and, further, that the apparent constancy of the velocity constant when so corrected reported by Kiss and his co-workers is due to errors in the equations used and in the choice of the equilibrium constant.

The equilibrium

$$\mathrm{I}_2 + \mathrm{I}^- \rightleftarrows \mathrm{I}_3^- \tag{6}$$

has been the subject of considerable work by Bray and MacKay[6] and more recently by Jones and Kaplan.[7] The only true equilibrium constant which can be discussed in this case is the one in terms of the activities of the three substances. The equation is

$$K_a = \frac{a_{\mathrm{I}^-}a_{\mathrm{I}_2}}{a_{\mathrm{I}_3^-}} = \frac{C_{\mathrm{I}^-}C_{\mathrm{I}_2}}{C_{\mathrm{I}_3^-}} \times \frac{f_{\mathrm{I}^-}f_{\mathrm{I}_2}}{f_{\mathrm{I}_3^-}} \tag{7}$$

where a represents activities, C concentrations and f activity coefficients. If it may be assumed that $f_{\mathrm{I}_2} = 1$ and that $f_{\mathrm{I}^-}/f_{\mathrm{I}_3^-} = 1$ or *const.* the ordinary equilibrium equation

$$K = \frac{C_{\mathrm{I}^-}C_{\mathrm{I}_2}}{C_{\mathrm{I}_3^-}} \tag{8}$$

is obtained.

---

[6] Bray and MacKay, THIS JOURNAL, 32, 914 (1910).

[7] Jones and Kaplan, *ibid.*, 50, 1845, 2066 (1928).

Bray and MacKay fixed a_{I_2} in their experiments by keeping the solution saturated with iodine. By making the assumptions that $f_{I^-}/f_{I_3^-} = 1$ and that the concentration of free I_2 in a solution of potassium iodide is the same as in pure water, 0.000136 mole per liter, they found that the values of K in Equation 8 increased steadily from 0.00131 in 0.1 molar potassium iodide to 0.00150 in 0.001 molar potassium iodide and an extrapolated value of 0.00153 for pure water (at 25°). Jones and Kaplan fixed a_{I_2} in the potassium iodide solutions by equilibrating the latter with solutions of iodine in water of known concentration and vapor pressure. Their solutions were not saturated with iodine and they obtained for potassium iodide solutions of concentration from 0.01 to 0.333 molar values of the equilibrium constant in Equation 8 varying slightly around 0.00140 at 25°.

In order to obtain these values for the equilibrium constant K, however, it is necessary for all of these investigators to assume that

$$(C_{I_2})_{H_2O} = (C_{I_2})_{KI\ Soln} \text{ or } (f_{I_2})_{H_2O} = (f_{I_2})_{KI\ Soln}.$$

While it is thermodynamically true that $(a_{I_2})_{H_2O} = (a_{I_2})_{KI\ Soln.}$ under these conditions, some doubt must rest upon the other assumption, although there is no apparent way *at* present to avoid making it; no experimental evidence is available for its support.[8]

From the preceding discussion it will be seen that any correction introduced into the reaction velocity equation will in itself involve uncertainties except in those cases where the reaction mixture is saturated with respect to iodine over the entire course of the reaction. Even in the latter case it will still be uncertain that $f_{I^-}/f_{I_3^-} = 1$ or a constant. It is worth noting that Lewis and Randall[9] do not make either assumption, although it is evident that both are approximately true.

As a matter of practical expediency it will be necessary to set aside these theoretical objections, since more exact information on the various terms of Equation 7 is not available, and to assume that over the range of potassium iodide concentrations concerned in the present paper, the series of values for the equilibrium constant K are as determined by Bray and MacKay.[10]

---

[8] That the present situation is anything but clear may be seen from the fact that the equilibrium constant K in Equation 8 increases as the concentration of potassium iodide decreases from 0.01 to 0.001 molar, while in barium iodide solutions over the same range of concentrations K increases. Cf., footnote 10 and Pearce and Eversole, *J. Phys. Chem.*, 28, 245 (1924).

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 527.

[10] Lewis and Randall, ref. 9, and Jones and Hartmann, THIS JOURNAL, 37, 241 (1915), have applied small corrections to these values or the data which determine them. The differences are immaterial over the range considered A part of the table given by Bray and MacKay is

$KI + KI_3$	=	0.010	0.005	0.002	0.001	0.000
$C_{I^-}/C_{I_3^-} = K'$	=	1.06	1.08	1.11	1.14	(1.16)
$K = K'C_{I_2}$	=	0.00140	0.00143	0.00147	0.00150	(0.00153)

Letting the initial concentration of potassium persulfate be *a* moles per liter and that of potassium iodide be $2a$, then according to the stoichiometric equation, for every x moles per liter of persulfate used in the reaction, $2x$ moles of potassium iodide will also disappear and x moles of iodine be produced. Since the equilibrium constant may then be expressed by the equation

$$K = \frac{C_{\mathrm{I}^-}}{C_{\mathrm{I}_3^-}} C_{\mathrm{I}_2} = \frac{(2a - 2x - C_{\mathrm{I}_3^-})\,(x - C_{\mathrm{I}_3^-})}{C_{\mathrm{I}_3^-}}$$

we find for the concentration of tri-iodide ion at any time during the reaction

$$C_{\mathrm{I}_3^-} = \frac{K + 2a - x}{2} - \sqrt{\left(\frac{K + 2a - x}{2}\right)^2 - 2x(a - x)} \tag{9}$$

If the effect of the tri-iodide ion is merely to reduce the concentration of iodide ion, then the bimolecular reaction velocity equation becomes

$$-\frac{\mathrm{d}C_{\mathrm{S_2O_8}^{--}}}{\mathrm{d}t} = k_1 C_{\mathrm{I}^-}\, C_{\mathrm{S_2O_8}^{--}} = k_1(2a - 2x - C_{\mathrm{I}_3^-})(a - x) \tag{10}$$

The corresponding equations given by Kiss and Zombory[4c] are

$$C_{\mathrm{I}_3^-} = \gamma = \frac{K + 2(b - x) + x}{2} \sqrt{\frac{K + 2(b - x) + x}{2} - 2(b - x)}$$

and

$$2k_1' = k_1 = \frac{dx}{dt}\,\frac{1}{(a - x)\,(b - x - \gamma)}$$

where *a* is the molar concentration of potassium persulfate, $2b$ is the molar concentration of potassium iodide and x is "the amount of I_2 formed." These equations are either grossly misprinted or derived upon some unknown basis. That they are incorrect may be seen in the case of the first by setting $x = 0$, for which it does not yield $C_{\mathrm{I}_3^-} = 0$ as demanded by experiment and theory. The second equation can be correct only if $\gamma = C_{\mathrm{I}_3^-}$ really means twice the tri-iodide concentration, in which case the first equation becomes still more puzzling.

The equation for the tri-iodide correction given by Kiss and Bruckner[4a] is

$$C_{\mathrm{I}_3^-} = y = \frac{b + K}{2} - \sqrt{\frac{(b + K)^2}{4} - x(b - x)}$$

where *b* is the equivalent concentration of potassium iodide and x is, presumably, equivalents of iodine formed. This equation results if in Equation 8 we put $C_{\mathrm{I}^-} = b - x - y$ and $C_{\mathrm{I}_2} = x - y$. The latter, however, means that the equivalent concentration of iodine is inserted into Equation 8, which is unjustified in this case since the equilibrium constant used by these writers is in terms of molar concentrations. The correct equation with b and x as equivalent concentrations is

$$y = \frac{K + b - x/2}{2} - \sqrt{\left(\frac{K + b - x/2}{2}\right)^2 - \frac{x}{2}(b - x)}$$

The experimental results on the reaction between potassium persulfate and potassium iodide in solutions containing initially only these salts are given in Table I and graphically in Fig. 1, Curve 1. Table I summarizes the results of three independent experiments performed at different times with two different samples of each of the salts. The agreement between the results of the three experiments can be seen on the curves. The decrease in the value of k' is evident. These values of k' were calculated by means of the integrated form of Equation 2, which for this case becomes

$$k' = \frac{1}{2at}\,\frac{x}{a - x} \tag{11}$$

Since k' is only the average value for the reaction between the beginning of the reaction and the time stated, and since several of the velocity equations which will be used cannot be integrated, it will be more convenient for purposes of comparison to use values taken from the single curve representative of all the experimental values. These values are given in Table II. The slope of the curve at each of the various times

TABLE I

THE REACTION BETWEEN PERSULFATE AND IODIDE IONS, AT 25°, WITH NO IODINE PRESENT INITIALLY

KI = $2a$ = 0.01; $K_2S_2O_8$ = a = 0.005; x = I_2 produced = $S_2O_8^{--}$ consumed in moles per liter.

Time, min.	Expt.	x, moles per liter	k' from Eq. 11
100	4	0.000550	0.124
140	23	.000736	.123
160	24	.000825	.124
250	4	.001150	.119
300	23	.001296	.117
360	24	.001481	.117
420	4	,001640	.116
470	24	.001751	.115
530	23	,001847	.111
560	4	0.001944	0.114
680	24	,002155	.112
730	4	.002247	.112
785	23	.002318	.110
1280	4	.002892	.107
1300	24	.002905	.107
1580	4	.003122	.105
2080	4	.003388	.101

TABLE II

CALCULATION OF THE VELOCITY COEFFICIENTS FROM EQUATIONS 2 AND 10

$C_{KI} = 2a = 0.01\ M.\quad C_{K_2S_2O_8} = a = 0.005$ M

Time, min.	x, moles per liter	$-\frac{dC_{S_2O_8}}{dt}$ X 10^6	k in Eq. 2	$C_{I_3^-}$ from Eq. 9	k_1[a] in Eq. 10	$C_{I_3^-}$ Eq. 9, using $K = 0.0061$	k_1, Eq. 10, using $K = 0.0061$
0	0	(6.26)	(0.1253)	.....	...	....	...
60	0.000345	5.35	.1234	.000298	0.1275	0.00021	0.1263
100	.000548	4.82	.1214	.000473	.1283	.00032	.1263
200	.000972	3.77	.1162	.000818	.1296	.00054	.1243
400	.001583	2.57	.1101	.001261	.1350	.00079	.1246
800	.002352	1.46	.1040	.001688	.1526	.00098	.1275
1200	.002824	0.945	.0998	.001804	.1707	.00100	.1296
1400	.002994	0.795	.0987	.001811	.1796	.00099	.1314

[a] Using interpolated values for the equilibrium constant K.

was determined by finding the difference in the values of x at two times at equal time intervals above and below the desired time and dividing this difference by the total time interval. The velocity constant k in Col. 4 is calculated from the differential Equation 2. Since these values are obtained from the slopes of the curve at the individual points, they represent more nearly than the values of k' in Table I, the actual behavior of the velocity curve at the various times. The decrease in k is therefore very much more marked than that of k'.

The constant obtained in a comparable experiment by Price,[11] agrees very well with our value when the results are recalculated to a common basis and the effect of the slight difference in the ionic strengths of the solutions is taken into account.

Column 5 of Table II contains the concentrations of tri-iodide ion as calculated by Equation 9, using interpolated values for the equilibrium at the different concentrations of $KI + KI_3$. When this is taken into consideration by means of Equation 10, the resulting k increases approximately 40% during the first two-thirds of the reaction. Col. 8 contains values for the velocity constant calculated in the same way but setting[L2] $K = 0.0061$, the value used by Kiss and his co-workers. This particular value was determined for a special purpose in which a knowledge was desired of the tri-iodide equilibrium in a solution containing 1.65 molar potassium chloride and 0.1 molar hydrochloric acid besides iodine and potassium iodide. It has no significance in solutions such as used in the experiments under discussion[13] and by Kiss. Therefore, unless we are willing to assume that the values of the equilibrium constant as determined by Bray and MacKay are only about one-quarter of the true values,[14] we must conclude that (1) the constancy of k in Col. 8 is fortuitous,[15] and (2) the correction of the iodide-ion concentration by subtracting the concentration of the tri-iodide is not adequate to account for the experimentally determined velocities. The assumption made by Kiss and his co-workers on the basis of the constancy of k that the tri-iodide ion does not react with persulfate ion is unjustified.

---

[11] Cf. Price, Ref. **3,** p. **478,** Table 6.

[12] Brönsted and Pedersen, *Z. physik.* Chem., **103, 307 (1922).**

[13] In the present article no account has been taken of the possible effect of the $K_2S_2O_8$ and K_2SO_4 on the equilibrium constants because these substances, at the concentrations involved, have practically no influence on the solubility of iodine.

[14] This is entirely out of the question since their values are in good agreement with those of earlier workers such as Jakowkin and Maitland (for references and summary see Bray and MacKay, ref. 6, p. **915)** and those of the very recent work of Jones and Kaplan, ref. **7.**

[15] Kiss, Zombory and Bruckner found this constancy using $K = 0.0061$, presumably by applying the equations quoted above given in their articles. The fact that the present writers also obtain constant values for k by applying the correct equations makes the articles by Kiss and his co-workers only more difficult to understand.

The value of $-dC_{S_2O_8^{--}}/dt$ for t = 0 in Table II is, obviously, extrapolated. The value of k found from this is in good agreement with values obtained by several other less exact methods. Extrapolation of the values of k' from Table I gave a value somewhere between 0.124 and 0.126. Similar procedures using values of x from the curve and applying Equation 11 gave 0.1251 and again from the plot of k (Table II) 0.1260. From another method, to be described in the next section, also depending upon extrapolations, 0.1285 was obtained. Since the value of k at t = 0 represents the velocity constant of the reaction when complicating factors such as the tri-iodide equilibrium are negligibly small, it will be important in several parts of the article. For its value we shall choose k = 0.125.

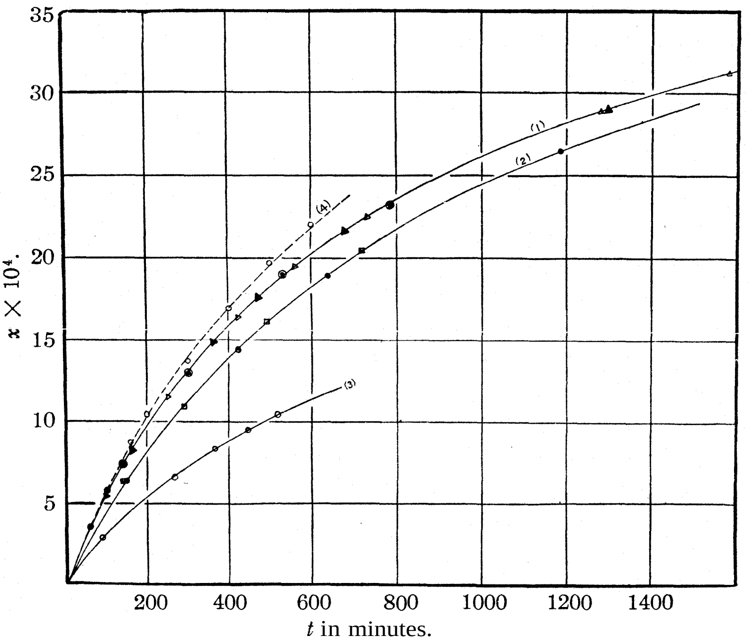


Fig. 1.—Curve 1, $K_2S_2O_8$, 0.005; KI, 0.01; I_2, 0, initially: △, June 19; ⊙, July 3; ▲, July 4. Curve 2, $K_2S_2O_8$, 0.005; KI, 0.01; I_2, saturated: ⊙, June 21; ⊡, July 3. Curve 3, $K_2S_2O_8$, 0.005; KI, 0.005; KNO_3, 0.005. Curve 4, I_2, 0 throughout (extrapolated).

D. Theory and Results of Experiments with Solutions Containing Iodine at the Beginning of the Reaction

All of the experiments by other investigators, as well as those reported above, indicate that the most troublesome factor in studying the reaction between $S_2O_8^{--}$ and I^- ion is the formation of I_3^- ion. The present writers believed that one way of clearing up the situation would be to make it worse. Accordingly, several experiments were performed in which various amounts of iodine had been added to the initial reaction mixture, in some cases the solutions being saturated with this substance throughout the reaction. The results for solutions saturated with iodine are given in Table III (experimental values) and Table IV (from a smoothed curve). The results for the unsaturated solutions are included in Table V, which will be discussed in detail later. Experiments 19 and 20 cited in Table III were performed several weeks apart, using different samples of all three substances. Several conclusions follow from these results: (1) the presence of the iodine has decreased the velocity of the reaction; (2) the reaction velocity constant shows a lower value than in Tables I and II but no drift in value regardless of the method of computation; (3) while in saturated solution of iodine in a given concentration of potassium iodide (over this range of concentrations) the actual concentration of iodide ion is only about one-half the amount if iodine were absent, the reaction proceeds at approximately 75% of the initial rate of the reaction without iodine present. The ratio of the two velocity constants and thus of the initial rates of reaction is 0.0958/0.1250 = 0.76; (4)

TABLE III

THE REACTION BETWEEN PERSULFATE AND IODIDE IONS, AT 25°, IN SOLUTIONS SATURATED WITH IODINE

KI = 0.01; $K_2S_2O_8$ = 0 005; I_2, saturated soln.

Time, min.	Expt.	x, moles per liter	k', Eq. 11	Time, min.	Expt.	x, moles per liter	k', Eq. 11
140	20	0 000632	(0.1033)	640	19	0.001900	0.0956
			(discarded)	720	20	.002047	.0960
150	19	,000631	.0963	1185	19	.002644	.0947
290	20	.001088	.0958	2070	19	.003345	.0977
425	19	,001431	.0943				
490	20	.001618	.0975			Av.	.0960

TABLE IV

CALCULATION OF VELOCITY COEFFICIENTS FROM EQUATIONS 11, 2 AND 10

C_{KI} = 0.01 M = 2a; $K_2S_2O_8$ = 0.005 M = a; C_{I_2} = saturated

Time, min.	x, moles per liter	k', Eq. 11	$-\frac{dC_{S_2O_8}}{dt} \times 10^6$	k, Eq. 2	C_{I^-},[a] used in Eq. 10	k_1, Eq. 10
60	0.000275	0.0969	4.35	0.0972	0.00487	0.1892
100	,000440	.0965	4.03	.0969	.00470	.1881
200	,000808	.0964	3.37	.0960	.00432	.1859
300	.001110	.0951	2.85	.0942	.00402	.1823
400	.001378	.0951	2.50	.0952	.00374	.1845
600	,001826	.0959	1.93	.0957	.00328	.1857
800	.002170	.0959	1.52	.0948	,00294	.1828
1000	,002441	.0953	1.25	.0952	.00266	.1838
	Av.	,0959		.0956		.1853

[a] Interpolated values of K' were used in obtaining these values.

if we are not to assume that tri-iodide ion or iodine "catalyzes" the reaction, then the tri-iodide ion must react with persulfate ion.

Before considering the last of these conclusions, it will be pertinent to discuss the reason for the constancy of the values in Cols. 5 and 7 of Table IV. The results of Bray and MacKay (see above) indicate that if the activity of the iodine in a potassium iodide solution is maintained at a constant value by saturating the solution with iodine, the ratio of iodide-ion concentration to tri-iodide-ion concentration remains practically constant over the range of potassium iodide concentrations involved.[16] In solutions in which the iodine activity is changing this is no longer true. Therefore whether iodide ion alone, tri-iodide ion alone, or both ions simultaneously react with persulfate ion, maintaining a constant iodine activity will immediately simplify the entire problem by making, practically, a single factor, that is, the total concentration of iodide plus tri-iodide ions in the solution, responsible for the actual concentration of each one.[17] If we may take the average ratio of the concentrations of these two ions in saturated iodine solutions, setting $C_{I^-}/C_{I_3^-} = K^r = 1.07$ for the range involved in Table IV, it can then be shown algebraically that, since

$$C_{I^-} + C_{I_3^-} = 2(a - x) \qquad (12)$$

Equation 10 may be transformed into

$$-\frac{dC_{S_2O_8^{--}}}{dt} = \frac{K'}{K' + 1} k_1 2(a - x)^2 \qquad (13)$$

By direct comparison of Equations 2 and **13** and inserting the values of K^r and k_1, we get

$$k = \frac{K'}{K' + 1} k_1 = \frac{1.07}{2.07} \times 0.1853 = 0.0958$$

These relationships thus explain the constancy observed among the values in Cols. 5 and 7 of Table IV, for it is evident that taking the tri-iodide concentration into consideration merely modifies Equation 2 by a constant factor when the solution is saturated with iodine throughout the reaction.

Table V summarizes the results of several experiments in which the initial concentrations of iodine were varied.[18] The values of x for each value of t were plotted against the total iodine concentrations ($I_2 + I_3^-$) at the same time and the curve extrapolated to zero iodine concentration

---

[16] See footnote 10.

[17] In investigations of the HIO_3–HI reaction Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926), found that saturating the solution with iodine simplified the problem.

[18] Only interpolated values are included in Table V. The experimental values on which Col. **3** is based were somewhat erratic, hence the values in this column were given less weight than those in other columns in the subsequent calculations. The values of k^t (Equation 11) calculated from the results in Cols. **3** and 4 decrease as the time increases but not quite as much as those given in Table I.

(Col. 6). The iodine concentrations for Col. 2 were obtained from the total iodide concentration $(2a - 2x)$ and the solubility table given by Bray and MacKay. The extrapolated values, while not very accurate (see Curve 4, Fig. 1) and becoming more uncertain for the higher values of t, give a constant which is in reasonably good agreement with those found by other methods. The reaction velocity curve obtained in this way is, of course, the result of a purely empirical process which gives merely the curve which would have been obtained from all the experiments cited above, including those in Table I, if the presence of iodine did not interfere with the reaction. By itself this method gives no indication as to the mechanism of the interference. The results in Table V directly contradict the statements made by Kiss and Zombory.[19]

TABLE V

THE VELOCITY IN SOLUTIONS CONTAINING IODINE INITIALLY. EXTRAPOLATION TO ZERO IODINE CONCENTRATION

	x					
Time, min.	$I_2 =$ *satd.* at $t = 0$	$I_2 = 0.001553$ at $t = 0$	In = 0.000729 at $t = 0$	$I_2 = 0$ at $t = 0$	*Extrapolated to* $(I_2) = 0$ at $t = 0$	k', Eq. 11
60	0.000275	0.000326	0.000332	0.000345	0.000351	0.126
100	.000440	.000516	.000535	.000548	,000563	.127
160	.000668	.000768	.000780	.000815	.000870	.132
200	.000808	.000922	.000935	.000972	.001042	.132
300	.001110	.001245	.001260	.001306	.001370	.126
400	.001378	.001515	.001537	.001585	.001690	.128
500	.001620	.001702	.001776	.001820	.001930	.126
600	.001826	.001952	.001978	.002022	.002200	.131
					Av.	.1285

Returning to the initial slope of the reaction between iodide and persulfate ions in solutions containing no iodine at the start, it can readily be seen that in a solution of the same ionic strength and concentration of persulfate ion, but with the molar iodide-ion concentration equal to instead of twice that of the persulfate ion, the initial slope of the curve would have been half the limiting value given in Table II, that is, 3.13×10^{-6}. An experiment with a mixture of 0.005 molar $K_2S_2O_8$, 0.005 molar KI and 0.005 molar KNO_3 gave 3.27×10^{-6} as an extrapolated value of $-dC_{S_2O_8^{--}}/dt$ at $t = 0$. This agreement is within the errors of experiment and extrapolation. The results of this experiment are plotted on Fig. 1 but not tabulated, since the work of Price is sufficient to establish the proportionality between the velocity and the concentrations of the reactants.

While the possibility that the tri-iodide ion may act as a catalyst for the iodide–persulfate ion reaction cannot be excluded entirely, the probability of such an effect seems to be very low, especially in view of the

---

[19] Ref. 4 *c*, pp. 227 and 229.

very satisfactory agreement to be shown below between experimental results and results of calculations based on the hypothesis that the tri-iodide ion itself reacts with the persulfate ion. The possibility that iodine may act as a catalyst must be rejected, however, on the grounds of the agreement just mentioned and because the behavior of the free iodine concentration could not possibly account for the observed results. In order to satisfy the latter, the free iodine concentration must vary in the same way as the tri-iodide ion concentration, that is, the ratio of tri-iodide-ion concentration to free iodine concentration should be constant. In saturated iodine solutions the concentration of free iodine is constant while that of the tri-iodide ion decreases continuously, but in the unsaturated solutions the tri-iodide concentration passes through a maximum during the course of the reaction.

On the other hand, if both iodide and tri-iodide ions react with persulfate ion and if the mechanism of the reaction between tri-iodide ion and persulfate ion is similar to that represented by Equations 3 and 4, the equation for the reaction velocity becomes

$$-\frac{dC_{S_2O_8^{--}}}{dt} = k_{I^-}C_{I^-}C_{S_2O_8^{--}} + k_{I_3^-}C_{I_3^-}C_{S_2O_8^{--}} \qquad (14)$$

For saturated iodine solutions the average velocity constant from Tables III and IV may be taken as 0.0958. The initial value for the unsaturated solutions from Table II is 0.125 which is the value of k_{I^-}. Again assuming that over the range of concentrations involved we may call the ratio $C_{I^-}/C_{I_3^-} = K'$ sensibly constant and equal to 1.07 in saturated iodine solutions, by combining this relation with Equation 8, we obtain from Equation 14

$$-\frac{dC_{S_2O_8^{--}}}{dt} = 2\left(\frac{K'k_{I^-} + k_{I_3^-}}{K' + 1}\right)(a - x)^2 \qquad (15)$$

By direct comparison with Equation 2, there results

$$k = 0.0958 = \frac{1.07 \times 0.125 + k_{I_3^-}}{1.07 + 1}$$

from which $k_{I_3^-} = 0.0645$.

For the reactions in which the solutions were not saturated with iodine, Equation 14 becomes

$$-\frac{dC_{S_2O_8^{--}}}{dt} = 2k_{I^-}(a - x)^2$$
$$-(k_{I^-} - k_{I_3^-})(a - x)\left[\frac{K + 2a - x}{2} - \sqrt{\left(\frac{K + 2a - x}{2}\right)^2 - 2x(a - x)}\right] \qquad (16)$$

The first term on the right is the simple expression for the case where no iodine is present at any point during the reaction; the second represents the effect of the tri-iodide ion. The term in square brackets is the concentration of tri-iodide ion, and for the experiments reported in Tables I and II it is identical with the values in Col. 5 of Table II.

TABLE VI

COMPARISON OR THE FINAL CALCULATED VELOCITY WITH THE OBSERVED VELOCITY

$C_{KI} = 2a = 0.01\ M$; $C_{K_2S_2O_8} = a = 0.005\ M$; $C_{I_2} = 0$ initially

Time, min.	$2k_{I^-}(a-x)^2$ × 10^6	2nd term in Eq 16 × 10^6	$-\frac{dC_{S_2O_8^{--}}}{dl}$ Calcd × 10^6	Obs. × 10^6
60	5.42	−0 OH4	5 34	5 35
100	4.96	− 127	4 83	4 82
200	4.06	− .199	3 86	3.77
400	2.92	− .261	2 66	2 57
800	1.75	− .270	1 48	1 46
1200	1.184	− .238	0 946	0 945
1400	1.006	− ,220	0 786	0 795

$k_{I^-} = 0.1250$; $k_{I_3^-} = 0.0645$. $K' = 1.07$

Values of the slopes of the velocity curve calculated by Equation 16 are given in Table VI, Col. 4 and for comparison the observed values are included in Col. 5. Col. 2 shows the slopes which would be observed if tri-iodide ions were not formed during the reaction. These calculations demonstrate conclusively that the observed reaction velocity is the sum of the velocities of two reactions, the first involving the iodide ions and the second the tri-iodide ions, and, furthermore, that the tri-iodide ion reacts at approximately one-half the rate of the iodide ion. The conclusion drawn by Kiss and Bossányi[4d] that the reaction between tri-iodide and persulfate ions is not appreciable at this temperature is unjustified.

Summary

The velocity of the reaction between iodide and persulfate ions is reinvestigated from the standpoint of the effect of tri-iodide ion formation. It is shown that earlier work on this reaction is insufficient and in some cases marred by too serious errors to be used for such a study.

Experiments have been made in solutions containing no iodine in the initial mixture and in solutions saturated with this substance. It is shown that by maintaining a constant iodine activity, it is possible to simplify the theoretical treatment and interpretation of the experimental data so that the observed reaction velocity may be analyzed into two parts, one being due to the iodide ion and the other to the tri-iodide ion.

NEW YORK, N. Y.

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

THE OXIDATION OF IODIDE ION BY PERSULFATE ION. II. THE EFFECT OF REMOVING THE PRODUCTS OF THE REACTION ON THE REACTION VELOCITY[1]

BY CECIL V. KING AND ERIC JETTE

RECEIVED SEPTEMBER 15, 1928 PUBLISHED APRIL 6, 1929

A. Introduction

The investigations reported in the first article of this series[2] showed that due to the formation and slower reaction of tri-iodide ion the reaction observed when solutions of potassium persulfate and potassium iodide are mixed is the sum of two concurrent slow reactions. It was also found that by means of an empirical procedure a velocity curve could be obtained in which the effects of the iodine and tri-iodide ion were eliminated. Further evidence of the correctness of these results was sought from experiments in which the iodine was more or less completely removed from the reaction by means of organic solvents and of a very rapid reaction. The earlier conclusions were also checked by repeating the experiments reported in the first article in solutions of considerably higher ionic strength. Experiments were likewise performed to show whether the removal of the other product of the reaction, the sulfate ion, had any effect on the reaction velocity. These experiments involved the determination of the salt effect due to the presence of several neutral salts.

B. Materials and Methods

The preparation of salts and solutions has already been described in the previous article. In some cases to be mentioned, however, it was necessary to use analyzed stock solutions for preparing solutions of the desired final concentration.

The organic solvents chloroform, carbon tetrachloride and carbon disulfide were redistilled, rejecting the first and last portions. The original materials were of "C. P." grade. The paraffin hydrocarbon was carefully treated to remove unsaturated compounds by shaking with concentrated sulfuric acid, boiling several times with alkaline permanganate solution and finally distilling; the portion boiling between 96 and 102" was collected for use

The sealed bulb method already described was used in all experiments excepting those where sodium hydroxide was present. Bulbs of 200-cc. capacity were used in the experiments with the solvent, each bulb containing 50 cc. of the reacting mixture (measured from a standard pipet) and 50 cc. of the solvent. Before sealing off, the bulbs were filled with nitrogen. The bulbs were placed in a device which turned them end over end in the thermostat at the rate of 10–15 turns per minute. Equilibrium between the iodine in the aqueous and solvent layers was thus established very quickly.

For the experiments involving sodium hydroxide, the reaction mixture was placed in a glass-stoppered bottle and a 50-cc. sample withdrawn from time to time. Five cc.

---

[1] Presented at the Swampscott Meeting of the American Chemical Society, September 12, 1928.

[2] Jette and King, THIS JOURNAL, 51, 1034 (1920).

of 1 molar sulfuric acid and 2 cc. of 1 molar potassium iodide was added and the iodine liberated by the iodate present titrated immediately with 0.01 molar sodium thiosulfate, using freshly prepared starch solution as indicator. Blanks were run on the reagents used. The temperature of the thermostat in which the reaction vessels were placed was 25.00 ± 0.01°.

C. Experiments with Organic Solvents Present

The results of attempts to find the influence of removing practically all of the iodine as fast as it was formed by means of organic solvents are summarized in Table 1. The symbols and concentration units are identical with those in the previous article. The value of k' is calculated from the integrated bimolecular equation

$$k' = \frac{1}{2at}\,\frac{x}{(a - x)} \tag{1}$$

The initial concentration of potassium persulfate is a moles per liter, of potassium iodide $2a$ moles per liter and x is the moles of persulfate ion consumed or iodine produced during the reaction. Several observations may be noted. (1) In all four cases the velocity curves (not plotted in Fig. 1) are above that in which no solvent was present. (2) For the first three solvents in the table the values of k' within each column are practically constant.[3] The average values of k' for the chloroform case is slightly above and for the paraffin hydrocarbon case slightly below the value 0.125 which was chosen in the previous article as the velocity constant for the iodide-ion reaction.

Table I

Reaction Velocities in Presence of Organic Solvents

$C_{K_2S_2O_8} = a = 0.005$ mole per liter; $C_{KI} = 2a = 0.01$ mole per liter

$CHCl_3$		CS_2		Paraffin hydrocarbon		CCl_4	
Time, min.	k', Eq. 1	Time, min.	k', Eq. 1	Time, min.	k', Eq. 1	Time, min.	k', Eq. 1
155	0.127	180	0.154	130	0.129	120	0.161
295	.127	320	.139	290	.122	250	.159
410	.130	530	.144	500	.120	550	.149
520	.131	710	.143	750	.119	815	.135
940	.128	860	.147	1440	.118	1325	.144
1560	.124	1550	.146	..	..	..	..
Av.	.128		.146		.122		.150

No satisfactory explanation has been obtained for the higher values of k' in the carbon disulfide and carbon tetrachloride experiments nor for the continuously decreasing values of Col. 8. The high values may be due to the specific effects of these substances in spite of their minute concentration in the aqueous layer. It is to be emphasized, however, that no far-reaching conclusions are to be drawn from the individual

---

[3] In their study of the HIO_3–HI reaction, Abel and Stadler, *Z. physik* Chem., 122, 49 (1926), found good pentamolecular velocity constants when the iodine was removed continuously by shaking with benzene.

numerical values in Table I due to an experimental difficulty involved to a greater or less, but unfortunately unknown, degree in each of the individual measurements. While the reaction bulbs were filled with nitrogen before sealing, so that no actual combustion of the vapors was observed, the local high temperatures to which the vapors of these organic substances were momentarily exposed always caused some decomposition and possibly some interaction with water vapor. Although the amount of these decomposition and interaction products was probably quite small, their nature is unknown. In some cases they may remove iodine from the solution, while in others they may liberate it from the iodide ions present or accelerate the reaction by the production of acids. In view of these conditions, the authors have limited the conclusions to be drawn from these experiments to the following statement. When the iodine formed by the reaction between persulfate and iodide ions is removed practically completely from the aqueous layer by means of an organic solvent for iodine, the values of k' obtained are generally more constant than when iodine is allowed to accumulate in the aqueous solution and in some cases the value of k' approaches closely the value of the true constant for the iodide–persulfate ion reaction.

D. The Reaction Velocity in the Presence of Sodium Hydroxide

In another series of experiments the iodine was removed from the system by means of sodium hydroxide. This method depends upon the fact that in the presence of a sufficiently high concentration of hydroxyl ions, iodine undergoes an internal oxidation-reduction according to the following equation

$$3I_2 + 6OH^- \rightleftharpoons 5I^- + IO_3^- + 3H_2O \qquad (a)$$

In combination with the iodide–persulfate ion reaction

$$S_2O_8^{--} + 2I^- \longrightarrow 2SO_4^{--} + I_2 \qquad (b)$$

the final result is the oxidation of iodide ion to iodate ion, the gross equation for which is

$$3S_2O_8^{--} + I^- + 6OH^- \longrightarrow 6SO_4^{--} + IO_3^- + 3H_2O \qquad (c)$$

In using these reactions the main assumption introduced was that the velocity determining reaction which, according to Bronsted, is

$$S_2O_8^{--} + I^- \longrightarrow (S_2O_8I)^{---} \qquad (d)$$

remains the same as in the absence of sodium hydroxide. As a corollary, it follows that regardless of its own mechanism, Reaction (a) must be assumed to proceed at a much faster rate than (d). It is also necessary definitely to assume that the final oxidation product of the iodide ion is the iodate ion. This last assumption has a very important effect on the equations for the reaction velocity, and the constancy of the velocity constant is a check on its validity. An unequivocal proof that (d) represents the velocity determining reaction is not possible, at any rate not from the present experiments. However, a close agreement in the values of the velocity constants obtained from two comparable experiments, in one of which sodium hydroxide was present while in the other it was not, would argue in favor of this view.

Two different velocity equations were used depending on the ratio of persulfate to iodide ions. If we let the initial molar concentration of potassium persulfate be a and that of potassium iodide be 2b then according to Reaction (c) above, when x moles per liter of persulfate ion has been reduced, $x/3$ moles per liter of iodide ion also has disappeared. We then get for the momentary concentrations of persulfate and iodide ions

$$C_{S_2O_8^{--}} = a - x \text{ and } C_{I^-} = 2b - \frac{x}{3}$$

From these and the velocity equation there is obtained

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}\, C_{I^-} = \frac{1}{3}\, k(a - x)\,(6b - x)$$

which upon integration and transformation to ordinary logarithms gives

$$k = \frac{6.909}{(6b - a)t} \log_{10} \frac{a(6b - x)}{6b(a - x)} \qquad (2)$$

Results of two experiments using this equation[4] are given in Tables II and III. The results in the latter are comparable with those in Table VII, since the ionic strength is the same in both The difference in the specific effects of nitrate and hydroxyl ions and to a lesser extent of potassium and sodium ions is evident from these two tables as well as the corresponding curves.

TABLE II TABLE III

REACTION VELOCITY IN THE PRESENCE OF NaOH

TABLE II

$C_{S_2O_8^{--}} = a = 0.00493\ M$
$C_{I^-} = 2b = 0.01\ M$
$C_{NaOH} = 0.05\ M$

Time, min.	k Eq. 2
122	0.176
190	.174
280	.175
390	.173
580	.173
670	.174
1270	.172
1590	.170
Av.	.173

TABLE III

$C_{S_2O_8^{--}} = a = 0.0493\ M$
$C_{I^-} = 2b = a = 0.01\ M$
$C_{NaOH} = 0.10\ M$

Time, min.	x Moles per liter × 10^3	k Eq. 2
62	0.600	0.211
130	1.174	.214
210	1.759	.217
340	2.476	.215
465	2.987	.213
1035	4.231	.208
1315	4.520	.211
	Av.	.213

---

[4] In these experiments the ratio of persulfate-ion concentration to iodide-ion concentration was not as simple as in the other experiments due to a slight error in making up one of the solutions. The simplification of Equation 2 for the case where the iodide concentration is $2a$ will be obvious.

TABLE IV TABLE V

REACTION VELOCITY IN THE PRESENCE OF NaOH

Table IV:

$C_{S_2O_8^{--}} = a = 0.005$ M
$C_{I^-} = a/3 = 0.00167$ M
$C_{NaOH} = 0.05$ *M*

Time, min.	k Eq. 3
240	0.166
510	.166
1160	.166
1685	.167
3013	.160
3375	.168
4580	.168
7350	.166
Av.	.166

Table V:

$C_{S_2O_8^{--}} = a = 0.005$ M
$C_{I^-} = a/3 = 0.00167$ M
$C_{NaOH} = 0.00833$ M

Time, min.	x Moles per liter $\times 10^3$	k Eq. 3
585	0.503	0.115
1215	.960	.117
1740	1.269	.117
3064	1.872	.117
3430	2.007	.117
4635	2.373	.117
7400	2.928	.115
11440	3.421	.114
	Av.	.116

Tables IV and V contain the results of experiments in which the initial molar concentration of potassium iodide was one-third of that of the potassium persulfate. The velocity equation for this case is somewhat simpler, namely

$$k = \frac{3}{at} \times \frac{x}{(a - x)} \tag{3}$$

The ionic strength of the solution used for the experiments in Table V is the same as for the experiments reported in Table I of the present article and Tables I and II of the previous article. The difference between the average value of k in Table V and the limiting value for the iodide–persulfate ion reaction obtained in the first article may be ascribed to specific effects of the sodium and hydroxyl ions, chiefly the latter, on the reaction velocity. The constancy of k in all four experiments given in Tables II, III, IV and V, and the agreement between the values of the constants in Table V with that of the limiting value (0.125) recorded in the previous article, are sufficient to justify the assumptions made regarding the velocity-determining reaction and the final oxidation product of the iodide ion.

E. The Effect of Removing the Sulfate Ion

Reaction (b) is, for all practical purposes, an irreversible reaction and therefore the presence of the final products of the reaction in actually attainable concentrations should have no measurable effect on completeness of the reaction. It was considered as a possibility, however, that the removal of the reaction products might increase the velocity. The removal of the iodine already discussed would obviously not serve as a test of this possibility.

The removal of sulfate ion is most easily accomplished by precipitation as barium sulfate. The addition of soluble barium salts increases the initial ionic strength, while the precipitation of the insoluble barium sulfate involves the continuous decrease of this factor. In order to reduce the complications involved in a large percentage change in ionic strength, the new series of experiments was performed keeping the iodide and persulfate concentrations the same as before but making the solutions also 0.10 molar with respect to potassium nitrate. The results of experiments containing potassium iodide, potassium persulfate and potassium nitrate are given in Table VII and will be discussed later. An additional complicating factor is present in that barium ions may have a specific effect on the reaction velocity quite apart from the influence due to the precipitation of barium sulfate. Therefore, the reaction velocities were also measured in the presence of magnesium and calcium salts. Since calcium sulfate is relatively insoluble, two series of experiments were made with solutions initially saturated with this salt, in one of them calcium nitrate also being present.

TABLE VI

EFFECT OF NEUTRAL SALTS ON THE REACTION VELOCITY

$K_2S_2O_8$ = 0.005, KI = 0.01 and KNO_3 = 0.10 molar in all experiments

Time, minutes	k' Eq. 1	Time, minutes	k' Eq. 1	Time, minutes	k' Eq. 1
$Mg(NO_3)_2$ = 0.01 M		$Ca(NO_3)_2$ = 0.01 M		$Na(NO_3)_2$ = 0.01 M	
0	(0.279)	0	(0.277)	0	(0.302)
100	.269	140	.266	140	.283
245	.258	280	,257	280	.268
455	.245	455	.248	440	.257
710	.233	765	.235	Curve 4	
Curve 3		Curve 3			
$Mg(NO_3)_2$ = 0.05 M		$Ca(NO_3)_2$ = 0.05 M		$Ba(NO_3)_2$ – 0.05 M	
0	(0.332)	0	(0.347)	0	(0.423)
100	.318	140	.324	140	.392
240	.301	280	,314	280	,369
450	.283	450	.301	440	.351
700	.271	765	.294	765	.327
Curve 5		Curve 6		Curve 7	
K_2SO_4 = 0.01 M		$CaSO_4$ (satd.)		$CaSO_4$ (satd.) + 0.01 M $Ca(NO_3)_2$	
0	(0.272)	0	(0.295)	0	(0.319)
110	.263	140	.280	100	.302
260	.264(?)	280	.269	240	.285
470	.241	380	.261	450	.269
710	.233	470	.259	650	.261
Curve 3		765	.246	800	.253

Results of all of these experiments are summarized in Table VI. It will be seen that barium nitrate has a definitely greater effect on the reaction velocity than the corresponding magnesium and calcium salts at the same concentration.[5] Whether the higher velocities thus ob-

---

[5] The titration values at various times for the 0.01 molar solutions of calcium nitrate and magnesium nitrate fell within experimental error on the *same* curve and

served are to be interpreted as due to the removal of the sulfate ion or to the specific effect of barium ions cannot be decided by means of such experiments but the velocities observed seem to be somewhat too great for the latter explanation alone to suffice. It may be observed that when the values of k' are plotted against *t* the resulting curves for the solutions containing barium ions drop more rapidly than those of the solutions containing magnesium and calcium. The curve for the solution saturated with calcium sulfate and containing 0.01 molar calcium nitrate shows the same behavior, being very nearly parallel to the 0.01 molar barium nitrate curve, although the curve for the saturated calcium sulfate alone decreases less rapidly and cuts across the latter. A very probable explanation of these differences may be found in the fact that in these solutions the ionic strength is decreasing appreciably while in the solutions in which no precipitation takes place there is a slight increase.

F. The Influence of Tri-iodide Ion Formation in Solutions of Higher Ionic Strength

Finally, the conclusions drawn in the first article of the series were checked by experiments in which the reaction velocities were made considerably higher than previously by using solutions containing 0.10 molar potassium nitrate. The experimental methods were the same as those of the earlier article. The results are given in Tables VII and VIII and Curves 1 and 6 on Fig. 1.

TABLE VII

REACTION VELOCITY IN 0.1 *M* KNO_3 SOLUTIONS

$K_2S_2O_8$ = 0.005 Molar
KI = 0.010 Molar
KNO_3 = 0.10 Molar
I_2 = 0 initially

Time, minutes	x moles per liter	k' Eq. 1
60	0.000670	0.258
140	.001290	.248
220	.001747	.244
355	.002278	.235
560	.002795	.226
1075	.003455	.208
1510	.003767	.202

TABLE VIII

REACTION VELOCITY IN 0.1 *M* KNO_3 SOLUTION SATURATED WITH I_2

$K_2S_2O_8$ = 0.005 Molar
KI = 0.010 Molar
KNO_3 = 0.10 Molar
I_2 = satd. initially

Time, minutes	x moles per liter	k' Eq. 1
120	0.000981	0.203
204	.001449	.200
360	.002071	.196
530	.002565	.199
1480	.003727	.198
	Av.	.199

In order to apply the equations already derived to the experiments, it was necessary to know the equilibrium constant for the reaction $I_2 + I^- \rightleftarrows I_3^-$ in solutions containing 0.10 molar potassium nitrate. The constant was obtained from measurements of the solubilities of iodine in

those for 0.01 molar potassium sulfate very slightly below this curve. Plots of k' against x gave the same results but the potassium sulfate results were somewhat more definitely lower than the others.

solutions containing 0.10 molar potassium nitrate besides potassium iodide at several different concentrations. The concentrations of the individual substances were calculated by the aid of the assumption that the solubility of free iodine in solutions containing potassium iodide is the same as in the pure "solvent," which in this case is 0.10 molar potassium nitrate. The solutions were saturated in sealed pyrex bulbs, the mixtures being rotated in the thermostat at 25.00 ± 0.01" for three days. The materials and technique were in other respects the same as in determining the initial concentrations of iodine in the velocity experiments already described. The results are given in Table IX, which is self-explanatory. It is noteworthy that potassium nitrate at this concentration has but little effect on the solubility of iodine and the equilibrium constant.

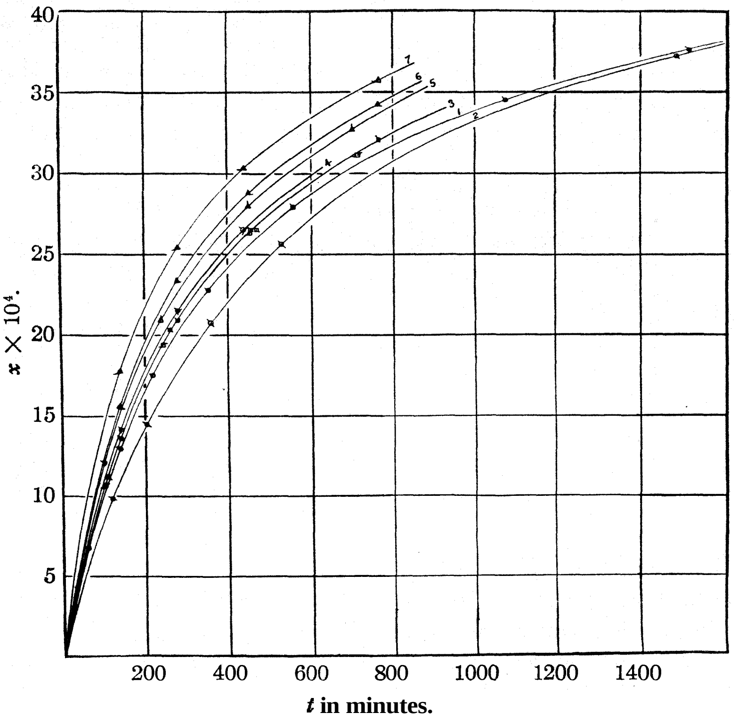


Fig. 1.—$K_2S_2O_8$, 0.005; KI, 0.01; KNO_3, 0.10. Curves: 1, salts alone; 2, with saturated iodine; 3, with 0.01 M magnesium nitrate, with 0.01 M calcium nitrate and with 0.01 M potassium sulfate; 4, with 0.01 M barium nitrate; 5, with 0.05 M magnesium nitrate; 6, with 0.05 M calcium nitrate; 7, with 0.05 M barium nitrate.

The value of k_{I^-} at $t = 0$ was determined by extrapolating the curves obtained by plotting k against t. The values of k **were** obtained from

TABLE IX

EQUILIBRIUM CONSTANT FOR $I_2 + I^- \rightleftharpoons I_3^-$

Moles KI per liter	Total I_2 = Ia + I_3^-	C_{I_2}	$C_{I_3^-}$	C_{I^-}	$K' = \frac{C_{I^-}}{C_{I_3^-}}$	$K = K'C_{I_2}$
0	0.001275	0.001275	.....	.....	...	.....
0.005	,003714	.001275	0.002439	0.002561	1.049	0.001339
.010	.006117	,001275	.004842	.005158	1.066	.001358
.020	.010983	.001275	.009708	.01029	1.061	.001352
				Av.	1.059	.001350

Table VII and also from the values observed (see Table X) from the smoothed curve. The extrapolation in the first case gave $k_{I^-} = 0.262$; in the second case, 0.269. The value $k_{I^-} = 0.265$ was chosen for subsequent use. The accuracy of the extrapolated values is somewhat less than in the case when no potassium nitrate was present due to the more rapid change in k with time. Accurate extrapolation of $dC_{S_2O_8^{--}}/dt$ was impossible. The value for $k_{I_3^-}$ is 0.169. The calculated results given in Table X were made with the same equations and with the same assumptions as those in Table VI of the first paper. The calculated slopes are all slightly higher than the observed values but the difference is easily within the error of determining k_{I^-}. The conclusion that the iodide and tri-iodide ions each react with the persulfate ions at characteristic rates is therefore confirmed.

TABLE X

EFFECT OF TRI-IODIDE EQUILIBRIUM ON REACTION VELOCITY

$K_2S_2O_8 = 0.005$ **Molar;** $KNO_3 = 0.10$ **Molar;** KI = 0.01 **Molar;** $I_2 = 0$ **initially**

Time, min.	x mole/liter (interp.)	$C_{I_3^-}$, moles per liter	$2k_{I^-}(a-x)^2 \times 10^6$	2nd term in Eq. 16 × 106	$-\frac{dC_{S_2O_8^{--}}}{dt} \times 10^6$ Calcd.	Obs.
60	0.000660	0.000566	9.98	−0.33	9.65	9.59
100	.001002	.000843	8.47	− .46	8.01	7.90
160	.001418	.001173	6.80	− .57	6.23	6.16
200	.001645	.001315	5.97	− .60	5.37	5.33
300	.002083	.001581	4.51	− .63	3.88	3.78
400	.002417	.001734	3.54	− .61	2.93	2.86
600	.002870	.001842	2.41	− .54	1.87	1.82

$k_{I^-} = 0.265$; $k_{3^-} = 0.129$; $k = 0.00135$

Summary

Further investigations were made on the reaction between iodide and persulfate ions. In the first article of the series it was found possible, by means of an empirical procedure, to obtain the velocity curve for the reaction if iodine or tri-iodide ion did not interfere with the reaction. These results have been confirmed by experiments in which the iodine was removed continuously from the reaction mixture by shaking with organic solvents and by reaction with sodium hydroxide. The effect of certain neutral salts on the reaction velocity was also determined.

It was found that removal of the sulfate ion as barium sulfate or calcium sulfate probably does not increase the velocity, although the effect of adding barium ion to the reacting mixture seems to be somewhat greater than it should if it is to be explained merely as a specific salt effect. Finally, the main conclusion of the first article, that is, that the observed reaction velocity is the sum of the velocities of the iodide and of the triiodide ions reacting with persulfate ion, was confirmed by measurements at considerably greater velocities.

NEW YORK, N. Y.

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

STUDIES ON SILICODUODECITUNGSTIC ACID.

I. THE PREPARATION OF SILICOTUNGSTIC ACID[1]

BY ARTHUR G. SCROGGIE[2]

RECEIVED SEPTEMBER 29, 1928 PUBLISHED APRIL 5, 1929

Silicotungstic acid originally prepared and described by Marignac[3] in 1863, has lately become an important analytical reagent on account of its ability to precipitate alkaloids. The present official method for the determination of nicotine is based on this property.

Drechsel[4] improved the original method of separating the acid by isolating it in the form of a complex which it formed with ether in the presence of a mineral acid. This procedure was only slightly modified by North and Beal,[5] who in 1925 extended the usefulness of this reagent by producing it in the form of a dry powder, stable in air and readily handled without decomposition. They also introduced a volumetric method, in which silicotungstic acid was used for the quantitative determination of alkaloids without previous isolation and purification. More recently Salzberg[6] has questioned the purity of the acid when prepared according to North's directions, and also North's assumptions with regard to the end-products obtained following decomposition of the acid by means of excess of alkali.

Because of the lack of agreement in the literature and the unsatisfactory status of the knowledge concerning silicotungstic acid, the researches of the present writer were undertaken with the following objectives: (a)

---

[1] Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

[2] This communication is an abstract of a portion of a thesis submitted by Arthur G. Scroggie in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Marignac, *Ann. chim. phys.*, [3] 69, 5 (1863).

[4] Drechsel, *Ber.*, 20, 1452 (1887).

[5] North and Beal, *J. Am. Pharm. Assoc.*, 13, 889, 1001 (1924).

[6] Salzberg, Master's "Thesis," University of Illinois, 1925; unpublished report, University of Illinois, 1925.

to investigate the possibility of forming the complex with new reagents and to determine the optimum concentrations for a maximum yield of acid, (b) to follow up the work of Salzberg and investigate quantitatively the methods of purification and dehydration of the acid, (c) to examine the methods of analysis of the acid and (d) to identify the end-products obtained by decomposing the acid with an excess of alkali.

1. Complex Formation.—Originally Drechsel had used ether and sulfuric acid to isolate the silicotungstic acid, but North had substituted hydrochloric acid for sulfuric, since an excess could be removed by heating. Rosenheim[7] has suggested that the compound concerned is of the oxonium salt type, but no records were found in the literature of investigations to establish this point or to find substitutes for the ether and acids previously used.

The method of extraction by a complex consists in adding ether to an aqueous solution of silicotungstic acid which contains a large excess of free mineral acid and then agitating the mixture. The complex sinks to the bottom as a heavy oily liquid and the excess of solvent floats on the surface of the aqueous layer.

To be suitable for the formation of a complex then, a solvent must be immiscible with and lighter than water, as well as a solvent for silicotungstic acid. If the oxonium salt theory is correct the solvent must also contain an oxygen atom.

A large number of solvents were tried in a qualitative way and the following facts established. Of the solvents containing oxygen, a number of esters, ketones and aldehydes could be substituted for ether, but ethyl acetate was the only one that seemed to merit quantitative investigation; a number of other solvents, including the lower alcohols, ketones, etc., were miscible with water and could not be used; acetic acid in addition to miscibility with water did not dissolve silicotungstic acid. Of the solvents which do not contain oxygen none was found to be satisfactory since they did not dissolve silicotungstic acid. These included petroleum ether, benzene, toluene, chloroform, carbon tetrachloride and carbon disulfide.

These results are in agreement with the work of Baeyer and Villiger[8] on oxonium compounds and are a general confirmation of this theory of the nature of the complex, but it was not found possible to isolate the pure compound for analysis.

Experiments demonstrated that nitric acid could be substituted for the usual precipitating agents, hydrochloric acid or sulfuric acid, but owing to its effect on the specific gravity of the solution it was not as efficient an agent as the ones previously used. Acetic acid would not

---

[7] Rosenheim and Jaenicke, Z. anorg. *Chem.*, 100,319 (1917)

[8] Baeyer and Villiger, *Ber.*, ***34*,** **2679** (1901)

cause the separation of the complex and was distinguished by its ability to prevent this action by the stronger acids. Sodium chloride in a concentration of 20% was found to be quite effective, particularly with ethyl acetate. Lithium chloride, nitrate and sulfate were all effective, but sodium sulfate, perchlorate and the salts of other metals could not be used. Just why the Li^+ is so much better than the Na^+ is not understood.

The presence of salt in a solution lowered the amount of mineral acid necessary to cause the separation of the complex, and a yield of 85–90% based on the weight of tungstate taken could be obtained using salt and ethyl acetate without any mineral acid. This method in fact is the most efficient for the extraction of the original process mixture which already contains 10 to 15% of salt. The combination ether and sodium chloride is not satisfactory, however, since the yield is only 50–60% of the theoretical. For purification of the acid by re-extraction from a solution which does not contain salt, ether and hydrochloric acid is the most efficient combination, and a yield of 98% can be obtained by adding an amount of hydrochloric acid equal to one-third of the original volume of the solution.

2. Methods of Analysis of the Acid.—As a preliminary step toward establishing the purity of the acid when prepared according to North's directions, methods of analysis were carefully examined. North dried the acid in an oven at 70° and then analyzed it in two ways: (I) by igniting the acid in a muffle furnace at a dull red heat, considering the loss in weight as water and the residue as anhydride; (8) by titrating the acid with standard alkali, using methyl orange as an indicator, which gave an end-point after the addition of four equivalents of base.

In the present investigation, the best temperature for ignition of the acid was found to be between 400 and 500°, since a sample of anhydride heated above this temperature underwent a progressive loss in weight depending, for any one sample, on the time arid temperature of ignition. Method II was improved by using very dilute alkali solutions, which gave sharper end-points, and the use of chlorophenol red as an indicator (PH range 5.0 to 6.0) because silicotungstic acid had been shown to give precipitates with methyl orange and most compounds containing basic nitrogen.

Salzberg used a third method of analysis which consisted in precipitating the silicotungstic acid with an excess of cinchonine solution, filtering the precipitate and igniting it to obtain the anhydride as a residue. In the hands of the writer this method gave results which varied slightly with different conditions and were uniformly higher than the value for the anhydride given by the first method mentioned. This method was not considered as reliable as the previous ones.

3. Purification of the Acid.—North dried the acid at 70° and obtained the following values for the percentage of anhydride: 94.58% (Method I), and 94.94% (Method II). He concluded that the acid had retained 5 molecules of water of hydration and had the formula $4H_2O·SiO_2·12WO_3·5H_2O$ (anhydride, 94.64%).

In the present investigation three samples of acid were prepared: (A) according to North's directions, (B) by re-extracting the above acid with ether (Salzberg's directions) and (C) by reforming the complex with ether twice. All samples were dried at 70° and analyzed, with the following results.

PERCENTAGE OF ANHYDRIDE

Sample	Method I, %	Method II, %	Mean, %
A	95.62	83.50	89.56
B	95.30	95.34	95.32
C	95.21	95.41	95.31

These results indicated an impurity in Sample A, the crude product, which was confirmed by precipitation of samples of the acid with cinchonine, filtering the precipitate and taking the filtrate to dryness in the presence of perchloric acid. The residue from Sample A, after adjusting for a blank on the reagents, was 1.2% of the sample weight, while the analyses of Samples B and C showed that within the limits of experimental error the impurity had been completely removed. These results confirmed the work of Salzberg and showed that a pure acid could be obtained only by following purification by reformation of the complex by means of ether and mineral acid, and also showed that a second reformation was not necessary.

4. Dehydration of the Acid.—In drying in an oven at 70° the acid, after a large initial loss, underwent a very gradual loss in weight which extended over several days and varied with the humidity of the atmosphere. Salzberg reported finding more moisture in a series of samples dried at 100° than he obtained from a series of samples dried at 70°. To solve these difficulties drying agents were tried as substitutes for the oven method and found to be far superior. Anhydrone or dehydrite under reduced pressure would dry small samples of the acid to constant weight in less than twenty-four hours. Hempel type desiccators were used and were evacuated by means of a Hyvac pump to a pressure of approximately 7 mm. Analysis of the acid as dried with different reagents gave the following percentages of anhydride as determined by ignition.

Drying agent	Dehydrite	H_2SO_4	$CaCl_2$	KOH *or* NaOH
Anhydride, %	95.40	95.50	95.31	95.25

All of these results correspond to an acid with somewhat less than the four molecules of water of crystallization expressed in the formula $4H_2O·SiO_2·12WO_3·4H_2O$, and would indicate that the last four molecules of water of hydration are retained quite persistently.

5. Decomposition of the Acid by Means of Excess of Alkali.—North assumed that the acid would be decomposed by a reversal of the process of preparation, which would require 26 equivalents of base per molecule of acid, according to the following

$$4H_2O{\cdot}SiO_2{\cdot}12WO_3 + 26NaOH \longrightarrow Na_2SiO_3 + 12Na_2WO_4 + 17H_2O$$

He carried out the determination by adding an excess of alkali, boiling the solution and back-titrating the excess with a standard acid, using phenolphthalein as indicator. His experimental values were 26 and 25.5 equivalents.

Salzberg, repeating the work with a purer acid, got values ranging from 23.5 to 24.5 equivalents and concluded that the theoretical value was 24 equivalents, which he explained by assuming that the silicic acid formed in the decomposition was not neutralized under the conditions of the experiment.

The writer by carrying out the decomposition in a system free from atmospheric carbon dioxide was able to get results that verified the latter theory. The experimental values obtained were 24.06 and 24.09 equivalents (assuming the acid to retain 4 molecules of water of hydration). The decomposition may therefore be represented by the following

$$4H_2O{\cdot}SiO_2{\cdot}12WO_3{\cdot}4H_2O + 24NaOH \longrightarrow H_2SiO_3 + 12Na_2WO_4 + 19H_2O$$

This decomposition is analogous to the decomposition of the yellow ammonium phosphate precipitate by alkali when the third hydrogen of phosphoric acid is not replaced by the alkaline metal. Assuming the theoretical ratio of 24 equivalents of base per molecule of acid, the reaction was used to analyze the acid, and it might be possible to work out *a* volumetric method for the analysis of the alkaloidal salts of silicotungstic acid as well, but this work was not undertaken.

6. **A** Modification of the Method of **Isolation** and Dehydration of **Silicotungstic** Acid.—As a result of these investigations, the writer would amend North's directions for the preparation of the acid as follows. Extract the original process mixture by adding an excess of ethyl acetate and 10–15% of common salt; dissolve the complex obtained in this operation in a liter of dilute hydrochloric acid (1 vol. of HCl to **3** vols. H_2O) and extract with an excess of ether which has been washed with 10% sodium hydroxide solution; take the complex to dryness on the water-bath, add water and take to dryness again; repeat this procedure till the residue no longer smells of volatile acid.

A very pure product can be obtained by recrystallizing this first yield from water; if the crystals are washed with an alcohol–chloroform mixture the loss by solution is not great. A current of air passed over the crystals for a few hours will dehydrate them sufficiently to permit of coarse powdering, after which they may be dried to constant weight by exposure to a good drying agent.

The acid produced in this way will absorb a small amount of moisture if exposed to the air.

The mother liquors, which are occasionally dark colored, may be readily clarified by heating with norite for a few minutes and filtering off the suspended matter.

The writer wishes to take this opportunity of thanking Dr. George D. Beal for suggesting this problem, and of expressing his regret that circumstances forced the latter's withdrawal from active participation in the work at such an early date.

Summary

1. The comparative value of different reagents for the formation of a complex with silicotungstic acid has been established and the probability that the compound formed is an oxonium salt has been indirectly confirmed.
2. Salzberg's conclusion with regard to the purity of the acid when prepared according to North's directions has been verified.
8. The truth of the assumption that the acid is decomposed by twenty-four molecules of base has been established experimentally.
4. The methods of analysis have been improved.
5. A new method of isolating the acid, depending on the formation of a complex with ethyl acetate, and a new method of dehydrating it have been proposed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. III. INFLUENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE[1]

BY RUFUS D. REED AND JAMES R. WITHROW

RECEIVED OCTOBER 20, 1928 PUBLISHED APRIL 5, 1929

We have shown the availability of zirconium sulfate as a reagent for potassium in the presence of sodium[2] and ammonium.[3] The less frequently occurring members of the fifth group, rubidium and cesium, both interfere with the detection of potassium by sodium cobaltic nitrite, perchloric acid or chloroplatinic acid. Lithium can be separated from ions of these elements by perchloric acid or chloroplatinic acid. Tread-

The authors are indebted to the Chemical Department of this University in that Professor Marion Hollingsworth of the Analytical Chemical Division of that Department furnished the rubidium and cesium chlorides used as the basis of part of this work.

[2] Reed and Withrow, THIS JOURNAL, 50, 1519 (1928).

[3] Reed and Withrow, *ibid.*, 50, 2985 (1928).

well-Hall states concerning sodium cobaltic nitrite and lithium,[4] "moderate amounts of alkaline earth elements or of lithium and sodium do not interfere." Concerning magnesium Prescott and Johnson[5] stated, "potassium and large amounts of sodium may be readily detected in the presence of magnesium." Yet because of interference with the detection of small amounts of sodium, magnesium is removed prior to testing for the fifth group, to determine whether these fifth group elements would interfere with the detection of potassium by zirconium sulfate. The sensitiveness of this reagent for potassium in the presence of lithium, rubidium, cesium and magnesium was therefore investigated.

The results indicated that in a 2-cc mixture, zirconium sulfate detected 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate, 16.6 mg. of rubidium sulfate or 11.6 mg. of cesium sulfate. It also detected 0.5 mg. or more of potassiuin in the presence of 50 mg. of magnesium sulfate. With no possibly interfering ions present, the zirconium sulfate reagent detected 0.5 mg. or more potassium.

The literature indicated that while Rosenheim and Frank[6] had prepared, "by the use of rubidium and cesium sulfates, compounds analogous in external appearance and in composition" to potassium zirconyl sulfate, no one had ascertained whether the presence of lithium, rubidium, cesium or magnesium would interfere with the reaction between potassium sulfate and zirconium sulfate, though the reference indicated the probability that they would interfere.

Experimental

In order to determine the effect of lithium, rubidium, cesium and magnesium upon the detection of potassium by zirconium sulfate, the following solutions were prepared.

Potassium Sulfate Solution and Zirconium Sulfate Solution.—These solutions were prepared in exactly the same way as described in the work on effect of ammonium ion on detection of potassium by zirconium sulfate.[2] The zirconium sulfate solution analyzed for **0.0871** g. of zirconium sulfate and an excess of 0.0395 g. of sulfate ion, due to excess sulfuric acid, per cubic centimeter.

Lithium Sulfate, Rubidium Sulfate, Cesium Sulfate and Magnesium Sulfate Solutions.—These solutions were prepared by dissolving potassium-free anhydrous salts in water and diluting to known volume.

Procedure.—Solutions containing known amounts of potassiuin and of either lithium, rubidium, cesium or magnesium sulfate were prepared by mixing known volumes of the proper solutions. The procedure of the test was the same as given in the preceding work.[2] The results appear in the table.

---

[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1920, Vol. I, p. **85.**

[5] Prescott and Johnson, "Qualitative Chemical Analysis," revised by J. C. Olsen, D. Van Nostrand Co., New York, 1918, p. 242.

[6] Rosenheim and Frank, *Ber.*, **38, 812–817 (1905).**

TABLE I

SENSITIVITY OF ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM

Total volume 2 cc. $Zr(SO_4)_2$ per test, 0.0871 g.

Expt.	K, g.	Sulfate	G.	Results and time for precipitation
1	0.0000	Li_2SO_4	0.0550	Cloudy, 3.5 hours; same in 5 hours at 0°
2	.0010	Li_2SO_4	.0500	Sl. cloudy, 1.5 hours; more cloudy than No. 1 in 5 hours at 0°
3	.0045	Li_2SO_4	.0500	Cloudy, 1.5 hours; more cloudy than No. 2 in 5 hours at 0°
4	,0082	Li_2SO_4	.0458	Sl. ppt., 1 hour; considerable ppt. in 2.5 hours at 0°
5	.0000	Rb_2SO_4	.0199	Cloudy, 5 hours at 0°
6	.0009	Rb_2SO_4	.0166	More cloudy than blank, No. 5, in 4.5 hours at 0°
7	.0018	Rb_2SO_4	.0166	Cloudy, 1.5 hours; ppt., 3.5 hours at 0°
8	.0031	Rb_2SO_4	.0142	Cloudy, 1 hour; ppt., 3 hours at 0°
9	.0066	Rb_2SO_4	.0166	Ppt., 0.5 hour at 0°
10	.0132	Rb_2SO_4	.0142	Cloudy, 0.5 hour at room temp.; sl. ppt, 1 hour, room temp.
11	.0000	Cs_2SO_4	.0127	Cloudy, 5 hours at 0°
12	.0005	Cs_2SO_4	.0116	No difference from blank No. 11, 5 hours at 0°
13	.0010	Cs_2SO_4	.0116	More cloudy than blank No. 5, 4.5 hours at 0°
14	.0045	Cs_2SO_4	.0116	Ppt., 1.5 hours at 0°
15	.0082	Cs_2SO_4	.0116	Opalescent, 1 hour at room temp., ppt., 0.5 hour at 0°
16	.0000	$MgSO_4$	.0550	Cloudy, 5 hours at 0°
17	.0005	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
18	.0010	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
19	.0045	$MgSO_4$	.0500	Cloudy and sl. ppt., 3.5 hours at 0°
20	.0082	$MgSO_4$	.0458	Cloudy, 1 hour; ppt., 2 hours at 0°

Discussion

The results indicate that zirconium sulfate will detect 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate (Expts. 1–4), 16.6 mg. of rubidium sulfate (Expts. 6–10) or of 11.6 mg. of cesium sulfate (Expts. 11–15). It did not detect 0.5 mg. of potassium in the presence of 11.6 mg. of cesium sulfate (Expt. 12). It detected 0.5 mg. or more potassium in the presence of 50 mg. of magnesium sulfate (Expts. 16–20). To detect 1 mg. of potassium in the presence of any members of the fifth group, a comparison with a blank run should be made concurrently. With lithium or magnesium present, comparison with a blank should be made in testing for 4.5 mg. or less potassium (Expts. 3 and 19).

Comparison of Reagents for Potassium.—In order to compare zirconium sulfate, sodium cobaltic nitrite, chloroplatinic acid and perchloric acid as reagents for the fifth group elements, a series of tests was made as tests are usually made in qualitative analysis—adding the reagent to the solutions to be tested. None of the four reagents gave a precipitate with 11% sodium acetate, 5.5% magnesium sulfate or 5.5% lithium sulfate. Sodium cobaltic nitrite solution gave a slight precipitate with a saturated lithium sulfate solution. Sodium cobaltic nitrite and chloroplatinic acid gave precipitates with 11% ammonium chloride, 1.92% rubidium sulfate and 1.16% cesium sulfate solutions as well as with 8.8% potassium sulfate solution. Perchloric acid gave a precipitate with the same solutions except the 1.16% cesium sulfate solution, but when a more concentrated cesium sulfate solution was prepared, it gave an immediate precipitate. *Zirconium sulfate gave a precipitate with the 8.8% potassium sulfate solution only.*

Reagents for the detection of potassium, other than zirconium sulfate, cannot be used in the presence of all members of the fifth group of metals. Sodium cobaltic nitrite, perchloric acid and chloroplatinic acid give a precipitate with rubidium and cesium as well as with potassium and ammonium. The perchloric acid method requires the use of absolute alcohol and the chloroplatinic acid requires the use of 80% alcohol to separate potassium from sodium and lithium.

Summary

Zirconium sulfate will detect 1.0 mg. or more of potassium in 2 *cc.* of reaction mixture in the presence of lithium, rubidium, cesium or magnesium ions, as well as those of sodium and ammonium. The detection of potassium by zirconium sulfate is accomplished without the use of alcohol or complicated procedure. It should always be used as the preliminary reagent, therefore, in looking for potassium, before going through the ordinary more complicated procedure.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

A STUDY OF THE DETERMINATION OF CHLORIDE IN BROMIDES

BY R. K. MCALPINE

RECEIVED OCTOBER 24, 1928 PUBLISHED APRIL 5, 1929

In 1926 Berg[1] introduced an interesting modification of the usual procedure for determining chloride in the presence of bromide by using acetone in aqueous solution to absorb the bromine set free in a differential oxidation process that employed potassium bromate in dilute sulfuric acid solution. The following equation shows the reaction involved:

$$6CH_3COCH_3 + 2KBrO_3 + 4KBr + 3H_2SO_4 = 6CH_3COCH_2Br + 3K_2SO_4 + 6H_2O$$

The chloride was then titrated by a modification of the Volhard method. The experimental data in Berg's article showed that the procedure recommended worked within moderate limits and it was suggested that the nephelometer could be used to determine very small amounts of chloride.

---

[1] Berg, *Z. anal. Chem.*, **64**, 342 (1926).

The present work was undertaken to replace potassium bromate with potassium permanganate and to extend the usefulness of the procedure in determining small amounts of chloride in bromides. Potassium permanganate has several advantages as an oxidizing agent. It is inexpensive, readily obtained free from halide, highly colored so that excess is easy to recognize, and easily reduced by hydrogen peroxide so the excess is simple to destroy.

Two general errors are possible in such work; one, incomplete removal of the bromide, leading to high results; the other, loss of chloride, leading to low results. Correct figures might be obtained by reducing both errors to negligible magnitude or from compensation of the two.

In the present work the chloride was determined gravimetrically, since such a precipitate could then be examined for bromide. The silver chloride was collected on a Jena filtering crucible, the weight of which is not affected by more than one or two-tenths of a milligram by the ordinary processes of filtering and washing. At the balance the more accurate procedure was adopted of using a counterpoise and weighing by substitution. This method of weighing easily reduces the ordinary error of four or five-tenths of a milligram to one-tenth of a milligram.

There were available as materials for study several commercial bromides of sodium and potassium and two specimens of potassium bromide of a high degree of purity. One of the latter had been prepared in connection with earlier work in the Laboratory[2] from recrystallized potassium oxalate and purified bromine; the other was made from Kahlbaum's potassium bromate that had been further purified by several recrystallizations using centrifugal drainage of the crystals. The potassium bromate was converted to bromide by careful heating in an electric furnace. A standard chloride solution was prepared from very pure sodium chloride, the concentration being determined by precipitation as silver chloride.

The accessory reagents used included potassium permanganate, sulfuric acid, nitric acid, silver nitrate, manganous sulfate, acetone, ether and hydrogen peroxide. Commercially available preparations were selected that were found on test to be either free from halide or to contain so small an amount that the total error for all combined would not exceed a tenth of a milligram. In the case of hydrogen peroxide, Merck's "Perhydrol" was used, being diluted to one-tenth its concentration and stabilized with diluted sulfuric acid.

Analytical Procedures

The analytical studies carried out may be divided into three general groups: (I) the use of permanganate in moderate excess in slightly acid solution, (II) the use of permanganate in slight excess in strongly acid

---

[2] Willard and McAlpine, This Journal, 43, 797 (1921).

solution and (III) the development of a concentration method for working with larger samples.

(I) The use of permanganate in slightly acid solution. The procedure first tried was patterned after that developed by Berg, using a moderate excess of potassium permanganate in relatively low acidities and with a large excess of acetone to react with the bromine. The reactions were carried out in a half-liter, glass-stoppered Erlenmeyer flask so that the final solution after addition of the silver nitrate could be shaken vigorously to coagulate the precipitate. Five ml. each of nitric acid (1:1) and of ether were added to assist this process.

By separate experiments with potassium bromide and sodium chloride solutions (see Table I) conditions were worked out such that the bromine from 50 mg. of potassium bromide could be converted completely to bromo-acetone and that 100 mg. of chlorine as chloride would suffer only the negligible loss of three- or four-tenths of a milligram. A quantitative determination of chloride in such a synthetic mixture gave a result containing no measurable error.

TABLE I

DETERMINATIONS OF CHLORIDE USING A MODERATE EXCESS OF POTASSIUM PERMANGANATE IN SLIGHTLY ACID SOLUTION

H_2SO_4 added Vol., ml.	Concn., *N*	Acetone ml.	KBr, g.	Cl–, g.	Time before reduction, min.	Error calcd. as Cl–, g.
50	1.5	25	0.050	0.00	2	+0.0007
50	1.5	25	.050	.00	5	.0000
50	2.0	25	.050	.00	2	.0000
50	2.5	25	.050	.00	2	.0000
50	1.5	25	.00	.1001	2	– .0003
50	1.5	25	.00	.1001	5	– .0004
50	1.5	25	.00	.0100	2	– .0001
50	1.5	25	.00	.0501	2	– .0002
50	1.5	25	.00	.2503	2	– .0006
50	2.5	25	.00	.0100	5	– .0004
50	2.5	25	.00	.0501	5	– .0005
50	2.5	25	.00	.2503	5	– .0011
50	1.5	25	.050	.1001	5	.0000

The directions worked out for the last determination in Table I were as follows. Use 25 ml. of acetone and 50 ml. of 1.5 *N* sulfuric acid in a total volume of approximately 85 ml. Add dropwise a 5% solution of potassium permanganate until the characteristic color persists, then 15 to 20 drops in excess. Let the solution stand for five minutes, reduce with 2 ml. of the hydrogen peroxide solution, add 5 ml. of nitric acid (1:1) and 5 ml. of ether, precipitate with silver nitrate, filter, wash with 1% nitric acid, dry and weigh.

On increasing the sample of potassium bromide to one gram the results of this method were not satisfactory. Qualitatively the reaction started smoothly with immediate decolorization of the permanganate and production of a yellow color of bromine that disappeared as the reaction with acetone took place; hydrated manganese dioxide soon started to precipitate and from then on the decolorization proceeded more and more slowly. The time required for disappearance of color when five drops of the reagent were added lengthened to one, two and even five minutes. At the latter stage the oxidation of the bromide was still far from complete. By continued addition of permanganate the test for bromide became faint, but by that time half an hour or more had been consumed with this operation. Even then quantitative tests showed that with 1 g. of potassium bromide and 100 mg. of chloride, the final precipitate gave a distinct test for bromide and yet its weight corresponded to a loss of over one milligram of chloride.

Further studies in dilute acid solution were therefore abandoned and the work entered its second phase.

(II) The use of permanganate in strongly acid solution. Since the oxidation potential of permanganate ion increases distinctly with the acidity of the solution, it seemed probable that conditions could be found such that with only a slight excess of permanganate the bromide would be completely changed to bromo-acetone without appreciable loss of chloride.

Test experiments showed that with increasing acidity, ranging from 3 to 10 N sulfuric acid, the volume of permanganate solution that was decolorized promptly by half a gram of potassium bromide increased very appreciably. At the same time precipitation of hydrated manganese dioxide decreased, finally ceasing entirely, and the color at the end-point became more definitely that of a dilute permanganate solution. These differences were distinct arguments in favor of using these newer conditions providing (a) the bromide was thus completely converted to bromo-acetone, (b) the chloride was not attacked, (c) the end-point

TABLE II

PERMANENCE OF THE PERMANGANATE END-POINT

Solution tested						
H_2SO_4 (1:1), ml.	$MnSO_4$ 0.3 N ml.	Acetone. ml.	Bromide added, g.	Chloride added, g.	$KMnO_4$ added, 5% soln.	Duration of color
50	0.0	25	0.0	0.0	1 drop	Permanent[a]
50	10.0	25	.0	.0	1 drop	Permanent[a]
50	0.0	25	.0	.10	1 drop	20 sec.
50	10.0	25	.0	.10	1 drop	5 min.
50	10.0	25	.0	.01	1 drop	18 min.
50	10.0	25	.05	.00	1.28 ml.	15 min.
50	10.0	25	.05	.01	1.30 ml.	10 min.

[a] In using the word permanent in this connection it should be noted that while one drop of the permanganate solution in 85 ml. produced a deep color in water alone, the color in these cases shifted rapidly to a light pink—deeper with manganous sulfate present than without—but when this light stage was once reached it did not undergo further change over a period of several minutes.

was reasonably permanent and, finally, (d) that the chloride could be quantitatively precipitated from such a solution. Quantitative experiments showed that these conditions were all fulfilled when one important modification was introduced, namely, the addition of 10 ml. of **0.3** N manganous sulfate solution to inhibit the oxidation of the chloride. In Table II are given data showing the satisfactory character of the end-point with manganous sulfate present.

The following quantitative procedure was finally adopted: measure out the volume of concentrated bromide solution to be analyzed, add 25 ml. of acetone, 10 ml. of 0.3 N manganous sulfate solution and 50 ml. of (1:1) sulfuric acid, cool in running water to 15–20°, add 5% potassium permanganate solution slowly with swirling until an end-point is reached, then add sufficient sulfuric acid to make the solution 11–11.5 N with respect to the acid, cool again and titrate to an end-point. Add one drop extra of the permanganate solution, let stand for one and a half to two minutes, reduce with **a** few drops of hydrogen peroxide, add ether and nitric acid as usual, precipitate with 0.25 N silver nitrate, adding 4 ml. excess, shake for one minute, filter, wash, dry and weigh.

Typical determinations using this procedure are given in Table III.

TABLE III

DETERMINATIONS OF CHLORIDE USING A SLIGHT EXCESS OF PERMANGANATE IN STRONGLY ACID SOLUTION

(a) Synthetic Mixtures

KBr taken, g.	**Chloride added, g.**	**Error calcd. as chloride, g.**	**Bromide test on ppt.**
0.10	0.010	0.0000	..
.10	.020	− .0001	Neg.
.10	.050	− ,0006	..
.10	.100	− .0008	Neg.
.50	.00	+ .0005	..
.50	.00	.0000	..
.50	.001	+ .0002	Neg.
1.00	.001	+ .0011	Pos.

(b) Commercial Salts

Salt	**Sample no.**	**Wt. of sample, g.**	**Chloride found, %**	**Bromide test on ppt.**
NaBr	1	0.500	1.00	Neg.
NaBr	1	1.000	1.10	Pos.
NaBr	1	1.000	1.05	Neg.
NaBr	2	0.500	0.69	Pos.
NaBr	3	.500	.29	Pos.
KBr	4	.500	.38	Pos.
KBr	5	.500	.40	Pos.

Preliminary quantitative experiments during the development of the above procedure using amounts of potassium bromide ranging from 50 mg. to 1 g. and with chloride added in quantities ranging from 1–200 mg. gave a maximum negative error of 2.4 mg. and a maximum positive error of **3** mg., calculated as chloride. The negative error was cut down by cooling the solution more carefully and the positive error was decreased by adding the extra drop of permanganate solution and letting stand a minute longer before reducing. With the procedure thus modified the errors on a 1-g. sample were found to lie within ±1 mg., an accuracy of 0.1%.

The work with half-gram and gram samples indicated that the rate of hydrolysis of the bromo-acetone might increase sufficiently with higher concentrations to offset any gain in accuracy that a larger sample might be expected to give. To show this more definitely two solutions of bromo-acetone of differing concentrations were prepared. Treatment with silver nitrate showed that silver bromide did precipitate more readily from the solution of higher concentration. Further, the rate of precipitation was not affected by an increase in the excess of acetone from ten-fold to two hundred and fifty-fold. In both solutions, however, the rate was decreased by an increase in acidity, falling off in one case to one-fifth by a change from 0.16 to 10 N, and in the other case to one-third by a change from approximately 2.6 to 11 N. The readiness with which opalescence developed even in the latter solution made it evident that the use of the nephelometer to determine small amounts of chloride could be of only limited value. Accordingly it was clear that an increase in accuracy would require a concentration method whereby most of the bromine could be removed before the acetone was added.

(III) Development of a concentration method. In removing most of the bromine by permanganate oxidation and direct volatilization it must be remembered that only half as much permanganate is required to convert bromide to free bromine as to change it to bromo-acetone. This is shown in the following equations

$$2KMnO_4 + 10KBr + 8H_2SO_4 = 5Br_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O \qquad (1)$$

$$4KMnO_4 + 10KBr + 10CH_3COCH_3 + 11H_2SO_4 = 10CH_3COCH_2Br + 4MnSO_4 + 7K_2SO_4 + 16H_2O \qquad (2)$$

In preliminary experiments there was added an amount of the 5% potassium permanganate solution that left about 0.2 g. of bromide unoxidized. The flask was then left on the edge of the hot-plate until the color became light yellow, cooled, treated with acetone and the rest of the operation carried out as before.

With 10-g. samples the final process of filtering out the silver chloride became slow. This was aggravated by the fact that the acetone interfered with the usual coagulation of a small precipitate so that the latter would occasionally mat in the filtering crucible and clog it seriously. This difficulty had been encountered in earlier work and largely overcome by using regulated suction such that the first filtering was complete in three to eight minutes. To reduce the volume sufficiently so that the same time range could be used here it was only necessary to substitute solid potassium permanganate for the solution and to use limited amounts of water, thus keeping the final volume within 100 ml. Since the mechanical difficulty referred to became evident only in the case of very small precipitates, one could eliminate it by adding a definite amount of chloride immediately before precipitating with silver nitrate. The final weight of precipitate could then be corrected for the amount of chloride added. This modification was regularly introduced when determining the small amounts of chloride that might be present in high grade analytical reagents.

Larger samples than 10 g. were not used because even with this amount salts frequently crystallized out when the acetone was added and the solution cooled. In such cases the salt redissolved when the precipitate was washed but the filtrate was usually cloudy and required refiltration.

A further source of error lay in the possible loss by volatilization of hydrogen chloride in the heating used to remove the bromine. Quantitative studies showed that with 100 mg. of chloride present and 50 ml. of (1:1) sulfuric acid, standing on the edge of the hot plate for one hour caused considerable loss of chloride. With smaller amounts of chloride the loss decreased and with the acidity lowered to 50 ml. of (1:3) sulfuric acid the loss became negligible.

The following is the procedure recommended for the concentration method: weigh out 10 g. of the bromide and 0.1 g. less than an equivalent amount of potassium permanganate (as calculated from Equation 1), transfer to a half-liter, glass-stoppered Erlenmeyer flask, add 40 ml. of water and 10 ml. of 0.3 *N* manganous sulfate solution and swirl for one or two minutes to dissolve the salts. Add 25 ml. of (1:1) sulfuric acid and place on the edge of the hot plate until the solution becomes light yellow (thirty to fifty minutes). Cool, add 10 ml. of acetone and sufficient sulfuric acid to make the solution 11 to 11:5 N with respect to the acid, cool again to 15–20' and treat dropwise with a 5% solution of potassium permanganate until one drop gives a permanent pink color. Add one drop more, let stand for one to two minutes, insert a tube into the flask above the solution and blow out any slight bromine vapors present; then reduce with a few drops of diluted Perhydrol solution. Add a measured volume of standard sodium chloride solution (20 mg. of chlorine), 5 ml. each of ether and of (1:1) nitric acid and precipitate with 0.25 *N* silver nitrate solution. Swirl the solution while the latter reagent is run in slowly until the solution shows a distinct decrease in opalescence, then add 4 ml. more of the reagent. Insert the stopper, shake for one minute, cool (to avoid loss when removing stopper), transfer the precipitate to a weighed filtering crucible, wash with 1% nitric acid, dry for three hours at 130°, cool and weigh. From the weight found subtract the weight corresponding to the amount of chloride added and calculate the percentage of chloride.

Typical determinations using this procedure are given in Table IV.

TABLE IV

ANALYSES OF BROMIDES BY THE PRELIMINARY CONCENTRATION METHOD

Salt analyzed	Wt. of sample, g.	Chloride found, %	Bromide test on ppt.
Best comml. NaBr	10.0	0.190	Slight[a]
Best comml. NaBr	10.0	.190	Faint
Best comml. NaBr	10.0	.189	Faint
Special KBr[b]	4.0	.014	Faint
Special KBr	8.0	.010	Faint

[a] Studies of known bromide–chloride mixtures showed that the precipitatt with silver nitrate gave a recognizable test for bromide with as low as 0.2 mg. of bromine. In testing for bromide the precipitate in the crucible was treated with a little water, plus a few drops of sulfuric acid and several tenths of a gram of granular zinc. After standing for four or five minutes the solution was filtered and the filtrate tested by adding a little more sulfuric acid, one or two drops of permanganate solution and then shaking out with carbon tetrachloride.

[b] This salt was the material prepared from potassium oxalate and bromine as earlier described.

Magnitude of Errors in the Final Procedure.—The positive error due to inclusion of silver bromide in the final precipitate might be caused by incomplete oxidation of the bromide or by partial hydrolysis of the bromo-acetone. The material presented in Table II (last two lines) showing the permanence of the permanganate end-point indicates that the bromide must be completely oxidized. It has already been shown that a bromo-acetone solution reacts slowly with silver nitrate but from the work done it would appear that this reaction was not sufficient to account for the slight tests for bromide obtained in the latter part of this study. In the precipitation of silver chloride, however, it would be possible for more silver bromide to be carried down than might separate from the solution by itself.

This point was tested experimentally by preparing a solution containing a little over 0.3 g. of bromine as bromo-acetone, adding 100 mg. of chloride and then, with other conditions the same as in the above determinations, the chloride was precipitated with silver nitrate. An excess weight was obtained corresponding to 0.6 mg. of bromine carried down. This amount would be sufficient to account for the bromide tests since examination of the method used in testing the precipitates showed it to be capable of recognizing as little as 0.2 mg. of bromine. The excess weight of the precipitate calculated as chloride would introduce an error of only 0.4 mg., and since the amount of bromo-acetone used was greater than would commonly be present at the end of the concentration method, this figure would appear to be a maximum for this error.

Loss of chlorine by volatilization of hydrogen chloride had already been reduced to negligible magnitude by control of the acidity during removal of the bromine. To determine directly the extent of oxidation by permanganate under the final conditions two test experiments were run. One hundred milligrams of chloride in a solution prepared as for a regular determination lost 0.4 mg. of chlorine on treatment at room temperature (22°) with one drop of 5% permanganate solution and letting stand for one and a half minutes before reduction. The second solution, cooled to 15°, was treated with two drops of the permanganate solution and let stand for two minutes before reduction. The loss this time was only 0.5 mg. This loss may be taken as a maximum when small quantities of chloride are to be determined, for in such cases one would never be dealing with as much chloride as was present in these experiments.

The errors of the method as finally developed may, therefore, be considered to lie within the limits of ±0.5 mg. and to be compensating in character.

Summary

1. A method has been worked out for the determination of chloride in bromides using potassium permanganate and acetone to convert the

bromide to bromo-acetone. The chloride is then determined gravimetrically as silver chloride,

2. The various errors of the process have been carefully studied.
3. On a 1-g. sample the accuracy of the procedure lies within 0.1%.
4. The rate at which a solution of bromo-acetone reacts with silver nitrate makes the nephelometric method inaccurate for small amounts of chloride.
5. By using a preliminary concentration method samples up to 10 g. can be employed for the accurate analytical testing of high grade reagents.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE TRANSFERENCE NUMBER OF BARIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

BY GRINNELL JONES AND MALCOLM DOLE

RECEIVED OCTOBER 31, 1928 PUBLISHED APRIL 5, 1929

Introduction

According to the classical electrolytic dissociation theory of Arrhenius the transference number of the ions should be independent of the concentration, but there are numerous well-established exceptions to the old rule. It has been the common practice to explain away the known variation of the transference number with the concentration as due to the presence of complex ions or as due to hydration in amounts which vary with the concentration, but these speculations have as a rule been qualitative only, with little serious attempt to develop a consistent quantitative theory or to express the variation of the transference number quantitatively as a function of the concentration.

The newer theory of complete electrolytic dissociation of Debye and Hückel gives a new point of view for the study of transference numbers. The new theory, unlike the old, does not neglect the electrostatic forces between the ions. According to this theory, at finite concentrations, the interionic forces tend to maintain a space lattice distribution of the ions and to oppose any disturbance of this arrangement by an outside electric field from an electrode and thus decrease the mobility of the ions. Therefore, the velocity of motion of an ion is not proportional to the potential gradient due to the outside electrode alone regardless of the concentration but is a decreasing function of the concentration. Debye and Hückel[1] have derived from this standpoint an equation for the variation of the equivalent conductance of strong electrolytes as a function of the concentration. This equation fits the facts fairly well at extreme dilutions

---

[1] P. Debye and E. Hückel, *Physik. Z.*, 24,185 (1923); 24,305 (1923); E. Hückel, *Ergebnisse der Exakten Naturwissenschaften*, 3,199 (1924).

(under 0.01 N) but fails quantitatively at higher concentrations. Owing to the abundance of relatively reliable conductance data and the scarcity of reliable data on transference numbers, especially at high dilutions, the proponents of this new theory have apparently confined their attention to conductance data in testing the predictions of the theory in regard to ionic migration velocities. The newer theory, however, predicts that the influence of interionic attraction on the mobility is not proportionally the same for all ions but is a function of the size of the ion, of the temperature and of the dielectric constant of the solvent, and especially of the valence. Therefore the new theory, unlike the old, would predict that the transference numbers of ions should be a function of the concentration. So far as we know no one has yet published the derivation from these new premises of an expression for the variation of the transference number as a function of the concentration, valence and nature of the ions.[2]

The present paper records the first results of an attempt to study experimentally the variation of transference numbers with concentration and to determine the factors which influence this variation.

Experimental Part

Analytical Method.—The best available barium chloride was dissolved in hot water, filtered, precipitated by adding pure, freshly distilled alcohol, dried in a centrifuge, recrystallized from water, dried in a centrifuge and finally dried in an electric oven at 120". Spectroscopic tests gave no evidence of the presence of strontium or calcium, although the original material when tested in a similar fashion showed the presence of strontium. Solutions were made up of approximately the concentration desired and the exact concentrations determined by analysis as described below.

The most exact determinations of the transference numbers of chlorides by the analytical method have been made by Washburn,[3] whose technique is a distinct advance over that of all earlier experimenters, but in spite of his fundamental improvements Washburn's method is involved, difficult, laborious and time consuming, and considerable skill and practice are needed to obtain reliable results. It should be especially noted that evaporation of the solutions during the operations of separating the electrolyte into five portions and filtering out the silver–silver chloride mixtures composing the electrodes, changes the concentration of the solution and thus introduces an error Every detail of manipulation must be planned to reduce this source of error as much as possible. The error due to unavoidable evaporation during manipulation can be minimized by using an apparatus of large volume of the anode and cathode chambers. For the anode Washburn recommends a Soxhlet extraction tube of filter paper filled with electrolytic silver crystals in which a coil of silver wire is buried. During the experiment silver chloride is formed on the silver wire and crystals, but contrary to Washburn's experience, we found that the silver chloride formed during electrolysis

---

[2] This has been done by the junior author, but since the conductivity data are also needed to evaluate the constants of the equation, the theoretical discussion is postponed until a subsequent paper when data on the conductivity and viscosity of barium chloride solutions will be presented and correlated with the transference data. See Malcolm Dole, Harvard Ph.D. "Dissertation," 1928.

[3] E. W. Washburn, THIS JOURNAL, **31**,322 (1909)

cemented the crystals together. During the mechanical disintegration of the anode loss by evaporation was unavoidable and thus made the solution stronger than it should have been.

This difficulty was overcome by the invention of a more satisfactory form of anode. A silver wire gauze was attached to a silver wire and rolled into a cylindrical coil of three layers about 1 cm. long and slightly less than the glass tube in diameter. The gauze was covered with an adherent but spongy coating of metallic silver by the pyrogenetic decomposition of silver oxide, thus producing a much larger surface than is available in the Washburn form of electrode. These anodes would carry a current of 0.1 ampere for eight hours without the slightest formation of acid in the electrolyte due to the evolution of oxygen instead of the formation of silver chloride, provided the potential gradient in the electrolyte did not exceed one volt per centimeter. At the beginning of the experiment the lower end of the anode is attacked and as it becomes covered with silver chloride the zone of the reaction gradually moves upward and at the end of the experiment the upper portion is being used. The potential necessary to cause oxygen evolution is approximately one volt greater than that required to change silver to the chloride. Therefore if the potential gradient in the solution exceeds one volt per centimeter, oxygen may be formed at the lower edge of the anode instead of chloride being formed one centimeter higher up on the electrode. In our apparatus the distance between the electrodes was about 100 centimeters. We found that if 100 volts were used, gassing would occur on the lower edge of the electrode before the silver on the upper part of the electrodes had been covered with chloride. By restricting the voltage used to 70 volts there was an adequate margin of safety to avoid gassing at the anode until its capacity had been fully used. With the more concentrated solutions this limitation was of no consequence because we found it best to limit the current to 0.1 ampere to avoid excessive heating and to avoid gassing at the cathode and 70 volts was not necessary to give 0.1 ampere. With 0.1 molal and weaker solutions this limitation to 70 volts limited the current that could be used.

With our new form of anode no filter paper is required. The silver chloride formed during electrolysis adheres firmly to the anode and yet the anode remains porous so that the weak electrolyte within the anode can readily be mixed with the anode liquid without disintegrating the anode by shaking and diffusion and without opening the anode chamber. At the end of the experiment the anode chamber filled with anode and anode electrolyte was weighed, then the anode removed intact, washed with water and dried in an oven without the loss of silver chloride. The rest of the manipulation is similar to that of Washburn except that no filtration of the anode liquid is required and therefore the amount of evaporation is much less than in his procedure.

After the new form of anode had been developed and the experimental technique seemed to be satisfactory in other respects and we were getting results from the anode side which seemed to be reliable, the results from the cathode side continued to be erratic. For the cathode we were using a silver plate covered with a layer of precipitated silver chloride in accordance with Washburn's recommendation.[4] We found that such an electrode would carry a current of 0.1 ampere without evolution of hydrogen or formation of alkali. Since we could find no evidence of any other abnormal reaction at this electrode we were at length forced to conclude that the difficulty was in the washing of the silver chloride for the cathode with the original solution and in the filling of the electrode chamber.

Repeated washing of the precipitate with the solution to be used improved the

---

[4] S. A. Braley and J. L. Hall, THIS JOURNAL, 42, 1770 (1920); S. A. Braley and R. F. Schueider, *ibid.*, 45, 1121 (1923), who used Washburn's method without modification, were unable to get reliable results with the cathode portions.

results somewhat but did not solve the problem. After much experimentation two different procedures were adopted, one suitable for the more concentrated solutions and the other suitable for the more dilute solutions. We tried a form of cathode somewhat similar to those used by Dewey[5] but modified so as to give a larger surface of silver. This larger surface of silver was obtained by decomposing silver oxide by heat. The first steps in making these cathodes were identical with the procedure used in making the anodes already described. Then the electrode was coated heavily with silver chloride by electrolysis in a chloride solution, washed and dried. These cathodes proved to be satisfactory for use with the dilute solutions (0.03 molal and under). With these solutions the current density was necessarily low on account of the high internal resistance and the necessity of limiting the potential gradient to one volt per centimeter as explained above. With the more concentrated solutions, however, these new cathodes failed because they would not carry the heavier currents needed without evolution of hydrogen. We were therefore forced to return to the Washburn type of cathode for use with the more concentrated solutions but were able to find a modification of the procedure which solved the difficulties described above.

The procedure finally adopted was as follows. A suitable quantity of silver nitrate was weighed out, dissolved in hot water, precipitated from hot solution by an excess of sodium chloride, thoroughly washed with hot water and then the supernatant water decanted. The damp precipitate was added to a glass-stoppered bottle containing all of the barium chloride solution to be used in the experiment and the whole thoroughly shaken. Of course, this changed the composition of the solution but no harm resulted, because it was later analyzed in the middle portions after the experiments. The bottle was allowed to stand until the precipitate had settled and most of the clear solution was decanted into a dry bottle. The precipitate was brought into suspension by shaking and the suspension poured into the cathode chamber through a funnel. The funnel was then withdrawn and the entire apparatus filled with clear solution and tightly closed. This procedure ensured that the barium chloride solution was uniform in composition throughout the entire apparatus. Certainly the agreement between the results obtained from the anode and cathode sides of the apparatus was greatly improved after this procedure was adopted. The five portions of the electrolyte were analyzed gravimetrically by precipitation of the chloride as silver chloride. This work must be done with great care because the errors in the analysis were magnified in the subsequent calculations, but this unusually accurate analytical method is so well known that it need not be described here.

The rest of the manipulation need not be described in detail since there were no significant variations from Washburn's procedure. In some cases the analyses of the anode middle and the cathode middle portions were omitted after it had been shown by measurements of the conductivity that these solutions were the same as the middle portion. During the electrolysis the apparatus was mounted in a thermostat at 25 ± 0.02°.

The results are computed on the assumption that the water does not move under the influence of the current and are, therefore, "Hittorf" numbers rather than "true" transference numbers in the sense that these terms are used by Washburn.

In the following table are given all the results that we believe to be reliable. It was not until Expt. 16 that our improved technique in handling the cathode was adopted. All earlier results obtained from the cathode side are rejected. Some of the later experiments had to be rejected because variations in the procedure were tried which proved to be unsuccessful. A few were lost by accident in the analysis. Some of the

[5] Jane Dewey, THIS JOURNAL, 47, 1927 (1925).

TABLE I
EXPERIMENTAL DATA

	Experiment no.								
	10	12	16	18	19	20	24	26	33
Molality (gr. mol/liter)	0.99	1.035	0.24745	0.10025	0.04985	0.05079	0.02395	0.01000	0.4987
Amperes	.1	.1	.1	.06	.03	.03	.015	.01	.10
Volts	27	27	60	70	70	70	70	64	25
Time in hours	7	7	7	10	8	8	7	5	7
Ag deposited in coul. from anode side	3.0792	2.9699	2.6585	2.0971	0.9588	0.9223	0.4487	0.2010	1.6704
From cathode side	3.0790	2.9694	2.6587	2.0972	.9586	.9230	.4487	.2010	1.6703
Wt. of anode portion	55.70	51.54	121.58	119.68	122.87	125.25	126.06	128.53	128.52
Wt. of cathode portion	71.09	73.45	121.80	121.06	Lost	123.90	120.83	120.83	133.61
Per cent. $BaCl_2$ in anode									
1st analysis	16.023	16.680	4.149	1.3658	0.7139	0.7521	0.3507	0.14253	9.1264
2nd analysis	16.020		4.147	1.3666					9.1257
Anode middle	17.570	Cond.	4.946	2.0546	1.0329	1.0505	Cond.	Cond.	9.5578
Middle middle									
1st analysis	17.576	18.275	4.948	Lost	1.0323	1.0512	0.4983	0.20846	9.5565
2nd analysis	17.571	18.282	4.946				.4984	Cond.	9.5574
Cathode middle	17.576	Cond.	4.946	2.0563	1.0308	1.0518	Cond.		
Cathode									
1st analysis	18.590	19.329	5.747	2.7384	1.3434	1.3534	.65207	.27800	9.9655
									9.9744
2nd analysis	18.579		5.745	2.7388					9.9614
									9.9672
									9.9780
									9.9769
Wt. $BaCl_2$ transferred									
From anode	1.0494	1.0073	1.0219	0.8428	0.3935	0.3786	.1871	.0849	0.6126
To cathode	(0.8654)	(0.9449)	1.0259	.8433		.3785	.1867	.0850	.6105
t_{Ba} from anode	.3530	.3514	0.3981	.4163	.4252	.4251	.4320	.4377	.3799
t_{Ba} from cathode	....	....	.3996	.4165	....	.4249	.4310	.4379	.3786
Accepted results	.3530	.3514	.3988	.4164	.4252	.4250	.4315	.4378	.3792
t computed from formula	.35317	.35119	.39878	.41612	.42525	.42504	.43202	.43748	.37928
Deviation $t_{comp.} - t_{obs.}$	+ .00017	− .00021	− .00002	− .00028	+ .00005	+ .00004	+ .00052	− .00032	+ .00008

missing numbers represent attempts to use 0.003 molal solutions but we were unable to obtain a reliable result with such dilute solutions. None of the results were rejected because they were not consistent with the new formula given below.

The Transference Number as a Function of Concentration.—The transference number, t, was plotted against the square root of the concentration, giving a smooth curve which was nearly straight but showed a definite curvature. It was then found that by plotting $1/(t+1)$ against $\sqrt{c}$ (Fig. 1, Curve I) a perfect straight line was obtained with all the experimental points falling on a straight line within the limit of error of the experiment. Then by the method of least squares the constants of the equation of this straight line were computed, giving

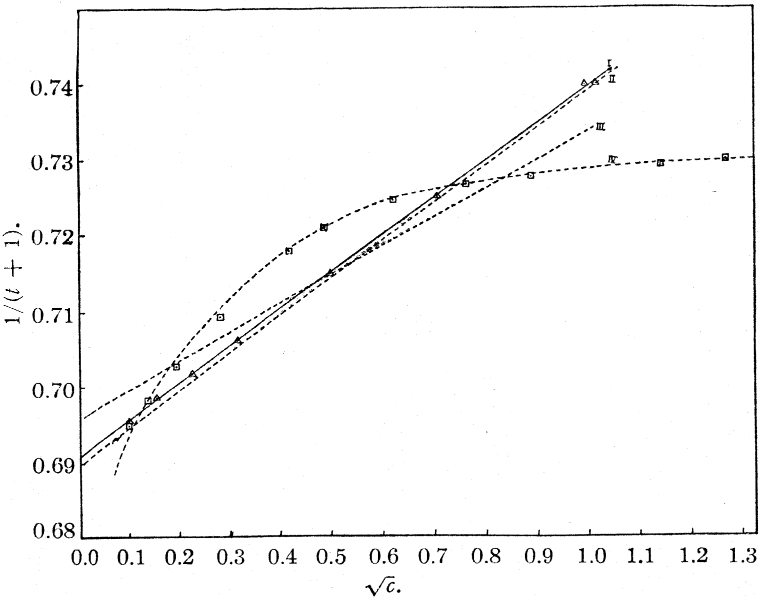


Fig. 1.—Reciprocal of transference number plus one, $1/(t+1)$, against square of the concentration, $\sqrt{c}$. The straight line I with points in triangles represents our data by the analytical method and is plot of Equation 1. The results obtained by the electromotive force method are represented by broken lines. The straight line II represents our data based on Equation 20. The straight line III represents our interpretation of Lucasse's data based on Equation 21. Curve IV with points in squares represents Lucasse's interpretation of his own data.

$$\sqrt{c} = \frac{20.6501}{t+1} - 14.2655 \qquad (1)$$

as the functional relationship between c and t. This is readily transferred into

$$(\sqrt{c} + 14.2655)(t+1) = 20.6501 \qquad (2)$$

This is the equation of a rectangular hyperbola between t and $\sqrt{c}$ with the asymptotes displaced from the axes at -14.2653 and -1. Another simple transformation gives

$$t = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1 \qquad (3)$$

The value of t at each concentration used in our experiments was then computed from this equation and is given in the second line from the bottom of Table I. The difference between the computed and observed values of t is given in the last line of Table I. As will be seen, the maximum deviation is +0.00052 in Expt. 24 and even here the computed result agrees exactly with the determination from the anode side, so that this deviation is clearly less than the possible experimental error. The average deviation is less than 0.0002. In view of the fact that most experimenters on transference numbers record their results only to the third decimal place this agreement is highly satisfactory. It should be noticed that the greater deviations occur in the dilute solutions where the experimental error is the greatest. Moreover, this equation holds exactly over the entire range of concentration from 0.01 to 1.035 mole per liter with no indication of systematic deviations in the more concentrated solutions. An additional reason for satisfaction is that the form of the function is such that there is no rapid change in slope as c approaches zero. It may therefore be used with considerable confidence for interpolation to obtain the value of the transference number at rounded concentrations and for extrapolation to infinite dilution. The values thus obtained are recorded in Table II. The value at infinite dilution is 0.4476.

TABLE II

TRANSFERENCE NUMBERS OF BARIUM IN BARIUM CHLORIDE SOLUTIONS AT 25° AT VARIOUS CONCENTRATIONS

c	0.000	0.001	0.005	0.01	0.025	0.05	0.10	0.25	0.5	1.0
t	0.4476	0.4444	0.4405	0.4375	0.4317	0.4253	0.4162	0.3986	0.3792	0.3528

Having discovered a new hyperbolic relationship between the transference number and the square root of the concentration which holds exactly in the case of barium chloride over a hundred-fold range in concentration, it becomes of much interest to determine whether or not this relationship is a general one. In the case of barium chloride one of the asymptotes of the hyperbola is at −1, but this may not be the case with other salts. An examination of the available data on transference numbers reveals very few cases in which the transference numbers have been determined over a wide range of concentration by the same method and at the same temperatures and by the same experimenter so that the data are comparable. The principal exceptions are the work of MacInnes and Reattie[6]

---

[6] D. A. MacInnes and J, A. Beattie, THIS JOURNAL, 42, 1117 (1920).

on lithium chloride, that of Lucasse[7] on barium chloride, strontium chloride and calcium chloride, that of Pearce and Gelbach[8] on barium chloride and that of Ferguson and Schlucter[9] on sodium hydroxide, all computed from the electromotive force of concentration cells with and without liquid junction. The transference numbers computed by these authors from their data do not show the same hyperbolic relationship between the transference number and the square root of the concentration which we have found for barium chloride. The results of Lucasse on barium chloride are shown in Fig. 1, Curve IV and, as will be seen, are widely different from the results which we obtained by the analytical method.

Experimental

Electromotive-Force Method.—In order to determine, if possible, the cause of the discrepancy, we undertook to measure the electromotive force of concentration cells with liquid junction similar to those used by Lucasse. The cells were of the flowing junction type used by Lamb and Larson.[10] In all of the experiments one-half of the cell contained 0.05 molal solution and the solution in the other half was varied in successive experiments from 0.001 to 1.000 molal. The electrodes were prepared by depositing silver chloride by a current of 1 milliampere for ten hours on a foundation of spongy silver formed by the pyrogenous decomposition of silver oxide. Electrodes when prepared in this way, then allowed to stand for several hours in a solution of potassium chloride or of barium chloride, nearly always agree within 0.00001 volt. We found that these electrodes could be transferred from one solution to another of different concentration and after standing for about one hour they gave definite and reproducible results.

For our final measurements a set of four electrodes was used. Two electrodes remained in the 0.05 barium chloride solution and the other two were used successively in the other solutions. These electrodes were allowed to stand for at least twenty-four hours in the solution under investigation in a thermostat before measurements were made. The difference between the pair in the same solution never exceeded 0.00003 volt and rarely exceeded 0.00001 volt. After this long-continued use in many different solutions they were all four put into a 0.05 molal solution of barium chloride and then the maximum difference between any two of the four was only 0.00003 volt.

Computation of Transference Numbers from the Electromotive Force of Concentration Cells.—The results shown in Table III were used in

---

[7] W. W. Lucasse, THIS JOURNAL, 47,743 (1925).

[8] J. N. Pearce and R. W. Gelbach, *J. Phys. Chem.*, 29,1023 (1925).

[9] A. L. Ferguson and A. W. Schlucter, *Trans. Am. Electrochem. Soc.*, 49,614 (1927).

[10] A. B. Lamb and A. T. Larson, THIS JOURNAL, 42,229 (1920).

TABLE III

ELECTROMOTIVE FORCE OF BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°

Ag, AgCl, $BaCl_2$ (c_1), BaCl (c_2), AgCl, Ag

c_2	c_1	$E_2 - E_1$ (1)	(2)	(3)	$E_2 - E_1$, mean
0.001	0.05	+0.0583	+0.0585	....	+0.0584
.005	.05	+ .03317	+ ,03333	+0.03329	+ .03326
.01	.05	+ ,02273	+ .02277	....	+ .02275
.025	.05	+ .00940	+ .00944	....	+ ,00942
.1	.05	− .00921	− .00923	....	− .00922
.25	.05	− .02127	− .02139	....	− .02133
.5	.05	− .03085	− .03077	....	− .03081
1.0	.05	− .04103	− .04101	....	− ,04102

preparing Fig. 2, in which $E_2 - E_1$ is plotted against log c_2 (points enclosed in circles). Then Lucasse's measurements (points enclosed in squares) were placed on the same plot by adding 0.02280 to each of his readings,

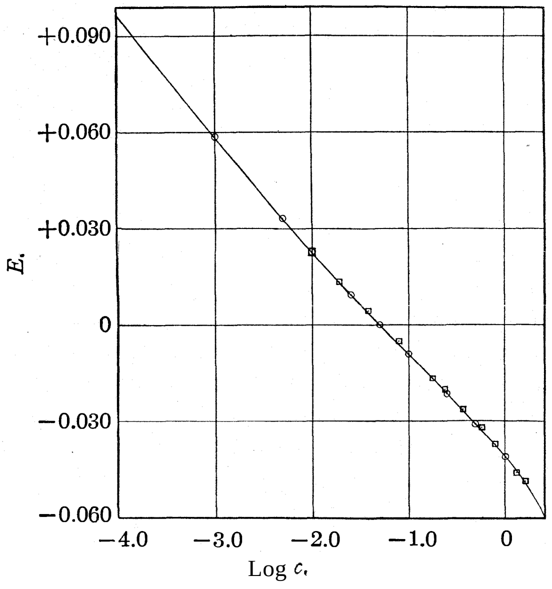


Fig. 2.—Electromotive force of barium chloride concentration cells with liquid junction, $E_2 - E_1$, against log c_2, all measurements being made against a solution having c_1 = 0.05 mole per liter. Points in circles represent our data. Points in squares represent Lucasse's data. The solid curve is the plot of Equation 16 which is derived from Equation 15 by substituting values of A and B determined from our analytical data and the values of N and P determined from Lucasse's data on concentration cells without liquid junction.

which refers them to the same arbitrary reference electrode ($c = 0.05$) as was used in our measurements instead of $c = 0.009968$ used by Lucasse. As will be seen, both sets of data fall on the same curve so well that the deviations are barely noticeable even on a large plot 50 cm. square, although Lucasse's data do not fit the curve as well as ours. We thus find ourselves in substantial agreement with Lucasse as to the experimental data. We have not verified his data on cells without liquid junction but in view of subsequent developments this seemed to be unnecessary.

The next step was a critical study of the method of computing transference numbers from the electromotive force of concentration cells. Lucasse employed a method modeled on that of MacInnes and Beattie for lithium chloride but modified disadvantageously so as to make it more dependent on plotting and less dependent on algebraic analysis. Lucasse first used his data on the electromotive force of concentration cells without liquid junction of the type Ag, AgCl, $BaCl_2$ (c_2), $BaHg_x$ —— Hg_xBa, $BaCl_2$ (c_1), AgCl, Ag to prepare a plot of activity coefficient against the square root of the concentration. From this plot he obtained by interpolation the activity coefficient at each of the different odd concentrations which were used in the measurements on concentration cells with liquid junction. The activity, a, was then computed and hence the quantity, A, which is arbitrarily defined as $1000a$. Then the electromotive force of concentration cells with liquid junction was plotted against log A. Up to this point he used the procedure of MacInnes and Beattie in principle, but with the difference that MacInnes and Beattie used identical concentrations in their cells with and without liquid junctions and therefore did not have to rely on values interpolated on plots. MacInnes and Beattie found that E could be expressed analytically as a binomial function of log A. This on differentiation gave a linear relationship between the transference number, t, and log A, which they used to compute t at any concentration within the range of their data. But this linear relationship cannot be applicable over the entire range of concentration because it leads to the result that as the concentration approaches zero the transference number must approach infinity.

Lucasse found that his curve between E and log A could not be expressed as a binomial and indeed was so complicated that he was unable to find the equation of the curve. He was therefore compelled to carry out by geometrical means the steps equivalent to those carried by MacInnes and Beattie by analytical methods. Lucasse measured the slope of his curves at various points and by dividing each value of the slope by the appropriate constant factor obtained a set of values for the transference number at various concentrations. These results are shown graphically in our Fig. 1 in the curve marked IV and, as will be seen, are not in agreement with our results obtained by the analytical method. Having confirmed the approximate reliability of Lucasse's measurements on the electromotive force of concentration cells with liquid junction, it seemed to us probable that the cause of the discrepancy was to be sought in errors introduced in the complicated method of plotting used by Lucasse. In this case the transference numbers must be inferred from the slope of the curves. The slope and especially the variation of the slope with concentration is greatly influenced by slight differences in judgment in drawing the complicated curves through the experimental points. We therefore undertook to develop an analytical procedure for computing transference numbers at any concentration from the data on electromotive force of concentration cells with and without liquid junctions.

The differential equation for the electromotive force of a concentration cell with liquid junction of the type Ag, AgCl, $BaCl_2$ (c + dc), $BaCl_2(c)$, AgCl, Ag is

$$dE = -\frac{3RT}{2F} t \, d \ln a \tag{4}$$

where t is the transference number of the barium ion at the concentration c and temperature T and a is the geometric mean activity of the ions in the same solution. The problem therefore is to express t and a as functions of the concentration and then integrate the resulting equation between the limits of concentration used in the measurements of electromotive force of concentration cells with liquid junction. If the values so computed agree with the observed voltages over a considerable range of concentration, the reliability of the expressions for t and a as functions of c may be regarded as confirmed.

It has been shown that for barium chloride we may write

$$t = \frac{1.4476}{1 + 0.0701\sqrt{c}} - 1 \tag{3}$$

or in generalized[11] form that

$$t = \frac{A}{1 + B\sqrt{c}} - 1 \tag{5}$$

The determination of the activity, a, as a function of the concentration, c, may be based on the measurement of the electromotive force of concentration cells without liquid junction. In a very important paper Hückel[12] has attacked the general problem of the variation of activity coefficient with concentration. He derives an equation (his Equation 97) for the

---

[11] This form is not fully generalized, as it may be necessary with other salts to replace the term —1 by another constant. The introduction of another constant would complicate the ensuing mathematical derivation and computations but would introduce no change in principle.

[12] E. Hückel, Physik. Z., **26**, 93 (1925). *See* also T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik.* Z., 29, 358 (1928), for another attempt to solve this general problem.

variation of activity coefficient with concentration which for a monovalent salt has the form

$$\log f = \frac{-0.354\sqrt{2c}}{1 + N\sqrt{c}} + Pc \qquad (6)$$

where N and P are constants for any given salt.[13] Hiickel gives computations and curves showing that this formula is consistent with the data of Allmand and Polack[14] on the electromotive force of sodium chloride concentration cells without liquid junction up to a concentration of 5.4 molal; and also consistent with similar data of MacInnes and Beattie[6] on lithium chloride up to *3* molal. For a divalent salt Hückel's equation reduces to the form $\log f = -1.734\sqrt{c}/(1 + N\sqrt{c}) + Pc$. The first step is to endeavor to select values for N and P which would be consistent with Lucasse's actual data. As first approximations for N and P we have used the values $N' = 2.175$ (taken from Harned's paper)[15] and $P' = 0.1475$.

The electromotive force of a concentration cell without liquid junction having a divalent salt such as barium chloride and electrodes reversible with respect to the anion such as Ag, AgCl electrodes is given by the equation

$$dE = -\frac{3RT}{2F}\,d\ln a = -\frac{3RT}{2F}\,2.3026\,d\,(\log c + \log f) \qquad (7)$$

$$dE = -\frac{3RT}{2F}\,2.3026\,d\left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) \qquad (8)$$

Integrating between the limits c_2 and c_1 gives

$$E_2 - E_1 = -3.4539\,\frac{RT}{F}\left[\left(\log c_2 - \frac{1.734\sqrt{c_2}}{1 + N\sqrt{c_2}} + Pc_2\right) - \left(\log c_1 - \frac{1.734\sqrt{c_1}}{1 + N\sqrt{c_1}} + Pc_1\right)\right] \qquad (9)$$

As a convenient abbreviation we will write $E = \phi(c, N, P)$, and refer to this as the Phi function. By the use of this equation $E_2 - E_1 = E_{\text{comp.}}$

---

[13] There are in use three methods of defining the concentration: mole fractions, moles per 1000 *g*. of water and moles per liter—with corresponding definitions of the activity coefficient. In Huckel's Equation 97 the activity coefficient is on the mole fraction basis, but owing to the uncertainty in the polymerization of water the mole fraction basis is inconvenient for practical use. Huckel uses the moles per liter basis in his practical numerical calculations to test his general formulas and this is the basis which we have adopted. It is easy to show by the use of Huckel's Equation 30 that if the activity coefficient is defined as the activity divided by the concentration in moles per liter, no change in the form of Equation 97 is necessary and that the only change required is a slight change in the numerical value of the coefficient of the term containing the first power of *c* (our P). But *P* is an empirical constant anyway. The mathematical steps in this transformation must be omitted to save space. See Harned, THIS JOURNAL, 48, 338 (1926), for some discussion of this question and for the corresponding transformation in terms of moles per 1000 g. of water.

[14] A. J. Allmand and W. C. Polack, *J. Chem. Soc.*, 115, 1020 (1919).

[15] H. S. Harned, THIS JOURNAL, 48, 338 (1926).

was computed for the actual values of the concentration used by Lucasse (after changing from m to c by the use of the following equation for the density of barium chloride solutions at 25° based on our own measurements: $d = 0.99707 + 0.1821c - 0.00407c^2$). These computed values were near enough to the observed values, $E_{\text{obs.}}$, to be encouraging but they probably were not within the experimental error and the deviations $\Delta E = E_{\text{obs.}} - E_{\text{comp.}}$ were apparently systematic. This indicated that N and P should be changed by some finite amount, ΔN and ΔP, and these values were found as follows. The rate of change of E with change in N and in P can be found by taking the partial derivatives of

$$E_2 - E_1 = \phi(c, N, P)_{c_1}^{c_2} \tag{10}$$

with respect to N and to P. Then

$$\Delta E = \left[\frac{\partial\phi\,(c, N, P)}{\partial N}\right]_{c_1}^{c_2}\Delta N + \left[\frac{\partial\phi\,(c, N, P)}{\partial P}\right]_{c_1}^{c_2}\Delta P \tag{11}$$

Each cell measured thus gives a linear equation between ΔN and ΔP with numerical coefficients and these equations can be solved by the method of least squares for ΔN and ΔP. The second approximations for N and P are then given by $N'' = N' + \Delta N$, and $P'' = P' + \Delta P$.

The values of $E_2 - E_1$ may then be recomputed and if the deviations are reduced but still significant and systematic, the process outlined above may be repeated. In this particular case the deviation equation takes the form

$$\Delta E = -\frac{3 \times 2.3026RT}{2F}\left[\left(\frac{1.734\sqrt{c_2}}{(1 + N\sqrt{c_2})^2} - \frac{1.734\sqrt{c_1}}{(1 + N\sqrt{c_1})^2}\right)\Delta N + (c_2 - c_1)\Delta P\right] \tag{12}$$

In this manner (using the points up to $m = 0.97$, only) we found $\Delta N = +0.052$ and $\Delta P = +0.0052$ and hence $N'' = 2.175 + 0.052 = 2.227$ and $P'' = 0.1475 + 0.0052 = 0.1527$. A repetition of the calculations gave $\Delta N = +0.0048$ and $\Delta P = -0.00004$ and hence $N''' = 2.227 + 0.0048 = 2.2318$ and $P''' = 0.1527 - 0.00004 = 0.15266$. Then f and E were computed with the equation $\log f = -1.734\sqrt{c}/(1 + 2.2318\sqrt{c}) + 0.15266c$, with the results shown in the following table.

TABLE IV

TEST OF HÜCKEL'S ACTIVITY FUNCTION FOR BARIUM CHLORIDE SOLUTIONS AT 25°

$$\log f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$$

Data by Lucasse on Electromotive Force of Cells without Liquid Junction

m	c	$\sqrt{c}$	$E_c - E_{0\,01}$, obs.	$E_c - E_{0\,01}$, comp.	ΔE volts	f
0.01	0.009968	0.09984	0	0	0	0.7244
.03016	.030048	.17334	0.03548	0.03612	−0.00064	.6136
.1004	.09984	.31597	.07420	.07406	+ .00014	.4942
.2978	.29452	.54270	.10921	.10914	+ .00007	.4163
.9710	.94073	.96992	.15322	.15325	− .00003	.4094
1.521	1.4459	1.2024	.17183	.17359	− .00176	.4516
1.650	1.5615	1.24962	.17713	.17759	− .00046	.4640

Having a new exact relationship between t and c from our own measurements by the gravimetric method and Hiickel's relationship between a and c, we are in a position to integrate the fundamental differential equation. Neither of these relationships was known at the time when MacInnes and Beattie published their important improvement over Nernst's method of computing transference numbers from the electromotive-force data.

$$dE = -\frac{3RT}{2F}\,t\,d\ln a \tag{4}$$

but

$$t = \frac{A}{1 + B\sqrt{c}} - 1 \tag{5}$$

and

$$\ln a = \ln c + \ln f = 2.3026(\log c + \log f) = 2.3026\left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) \tag{13}$$

$$-\frac{2F}{6.9078RT}\,dE = \left(\frac{A}{1 + B\sqrt{c}} - 1\right) d\left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) \tag{14}$$

By substituting $x = \sqrt{c}$, which simplifies the form of the integral, and integrating between the limits $x_2 = \sqrt{c_2}$ and $x_1 = \sqrt{c_1}$

$$Ez - E_1 = \frac{3RT \times 2.3026}{2F}\Big[-\frac{2APx}{B} + Px^2 - (2A - 2)\log x + \left(\frac{2}{2.3026} + \frac{}{(N - B)^2} + \frac{2AP}{B^2}\right) 2.3026 \log(1 + Br) - \left(\frac{1.734A}{N - B} - \frac{1.734}{N}\right)\left(\frac{1}{1 \mp Nx}\right) - \frac{}{(N - B)^2}\,2.3026 \log(1 + Nx)\Big]_{x_1}^{x_2} \tag{15}$$

As a convenient abbreviation we will write $E = \psi(x, A, B)$ and refer to this as the Psi function.

This equation, although complicated, is as rigid as the equations connecting t and a with c. If we substitute at 25° $3RT/2F$ 2.3026 = 0.088731 and $A = 1.4476$, $B = 0.07010$, $N = 2.2318$ and $P = 0.15266$; Equation 15 reduces to

$$E_2 - E_1 = +0.088731\Big[-6.30489x + 0.15266x^2 - 0.89512 \log x + 210.082 \log(1 + 0.0701x) - \frac{0.38420}{1 + 2.2318x} - 0.0867026 \log(1 + 2.2318x)\Big]_{x_1}^{x_2} \tag{16}$$

$E_2 - E_1$ was then computed for each of the barium chloride concentration cells with liquid junction measured by us and by Lucasse with the results shown in Tables V and VI.

These computed values against 0.05 molal barium chloride were then plotted ($E_2 - E_1$ against $\log c_2$) and are shown in the solid curve drawn in Fig. 2. This method of plotting was chosen because it gives a curve which is approximately a straight line, but when it is drawn on a large scale it is easily apparent that it is concave for small values of c, has a point of inflection near the middle and is convex for the higher values of c. As will be seen from Fig. 2, our experimental points and those of Lucasse

TABLE V

BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°. COMPARISON OF OUR OBSERVED VOLTAGE WITH THAT COMPUTED BY EQUATION 15

			First approximation, A = 1.4476, B = 0.07010		Second approximation. A = 1.460, B = 0.07135	
c_2	c_1	$E_2 - E_1$, obs	$E_2 - E_1$, comp	ΔE, obs comp	$E_2 - E_1$, comp.	ΔE
0.001	0.05	+0.0584	+0.05825	+0.00015	+0.05855	−0.00015
.005	.05	+ .03326	+ .03292	+ .00034	+ .03308	+ .00018
.01	.05	+ .02275	+ .02256	+ .00019	+ .02267	+ .00008
.025	.05	+ .00942	+ .00946	− .00004	+ .00951	− .00009
.05	.05	0	0	0	0	0
.10	.05	− .00922	− .00918	− .00004	− .00922	+ .00000
.25	.05	− .02133	− .02114	− .00019	− .02123	− .00010
.5	.05	− .03081	− .03066	− .00015	− .03078	− .00003
1.0	.05	− .04102	− .04094	− .00008	− .04109	+ .00007
			$\Sigma\Delta E$ =	+0.00018	$\Sigma\Delta E$ =	−0.00004

TABLE VI

BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°. COMPARISON OF LUCASSE'S OBSERVED VOLTAGE WITH THAT COMPUTED BY EQUATION 15

c_1 = 0.09968

			First approximation, A = 1.4476, B = 0.07010		Second approximation, A = 1.4372, B = 0.05409	
m	c_2	$E_2 - E_1$, obs.	$E_2 - E_1$, comp	ΔE, obs-comp.	$E_2 - E_1$, comp.	ΔE
0.01	0.009968	0	0	0	0	0
.01923	.01916	−0.00927	−0.00941	+0.00014	−0.00925	−0.00002
.03815	.03800	− .01852	− .01890	+ .00038	− .01859	+ .00007
.07977	.07937	− .02804	− .02874	+ .00070	− .02834	+ .00030
.1791	.1777	− .03941	− .03929	− .00012	− .03884	− .00057
.2426	.2403	− .04277	− .04330	+ .00053	− .04282	+ .00005
.3927	.3873	− .04907	− .04972	+ .00065	− .04926	+ .00019
.5971	.5854	− .05475	− .05550	+ .00075	− .05512	+ .00037
.8122	.7909	− .05995	− .05993	− .00002	− .05964	− .00031
1.372	1.311	− .06872	(− .06795)	(− .00077)	(− .06791)	(− .00081)
1.715	1.619	− .07134	(− .07158)	(+ .00024)	(− .07170)	(+ .00036)
			$\Sigma\Delta E$ =	+ .00224	$\Sigma\Delta E$ =	− .00009

fit the theoretical curve closely and follow the complicated curvature throughout the entire range in a way which supports the validity of our new function and shows that there is no real discrepancy between our data on the transference of barium chloride and by the analytical method and the electromotive-force data.

Although the deviations between the observed and computed voltages (ΔE of Tables V and VI) are so small as to be scarcely visible on a plot 50 cm. square, nevertheless computation shows that there are deviations which are apparently greater than the experimental error of the electromotive-force measurements. It will be seen from Table V that our deviations are apparently systematic, being positive in dilute solutions, negligible in middle concentrations and negative in the concentrated solutions, and that those of Lucasse are predominantly positive and larger than ours.

It now becomes of interest to reverse the computation described above and compute transference numbers from electromotive force alone and compare the results with the transference numbers obtained analytically. The numerical value of N and P is first computed from the voltage of concentration cells without liquid junction in the manner described above. Then as a matter of mathematical theory it would only be necessary to measure two different cells with liquid junction to make it possible to compute A and B and hence compute t at any concentration. But in practice it will be advisable to measure many cells covering the desired range of concentration and this requires that the data be treated by the method of least squares to find the best values of A and B. Moreover, the form of the function is so complicated that a simple numerical solution is not feasible. The problem can be solved, however, in a manner similar to that indicated above. First assume some value of A' and B' as a first approximation. Then compute E $= \psi(x, A', B')$ for each value of x used in the experiments and hence the deviation $AE = E_{\text{obs.}} - E_{\text{comp.}}$ Then

$$\Delta E = \left[\frac{\partial\psi\ (x,\ A',\ B')}{\partial A'}\right]_{x_1}^{x_2}\Delta A + \left[\frac{\partial\psi\ (x,\ A',\ B')}{\partial B'}\right]_{x_1}^{x_2}\Delta B \qquad (17)$$

Each cell measured thus gives a linear numerical equation with two unknowns, ΔA and AB, and these equations can be solved by the method of least squares. This gives a second approximation: $A^N = A' + \Delta A$ and $B'' = B' + \Delta B$.

This process can be repeated as often as is necessary, but unless the first approximation were greatly in error the third approximation will not differ from the second by a significant amount. In this particular case the partial derivatives take the form shown below

$$\begin{aligned}\Delta E = &+\frac{3RT}{2F}2.3026\Big[-\frac{2Px}{B} - 2\log x + \frac{2}{(2.3026} + \frac{}{(N-B)^2} + \frac{2P}{B^2}\Big)2.30261og\ (1+Bx)\\ &- \frac{1.734}{(N-B)(1+Nx)} - \frac{1.734B}{(N-B)^2}2.3026\ \log\ (1+Nx)\Big]_{x_1}^{x_2}\Delta A\\ &+\frac{3RT}{2F}2.3026\Big[+\frac{2APx}{B^2} + \Big(\frac{1.734B}{(N-B)^2} + \frac{2\times 1.734AB}{(N-B)^3} - \frac{4AP}{B^3}\Big)2.3026\log\ (1+Bx)\\ &+\Big(\frac{2A}{2.3026} + \frac{1.734AB}{(N-B)^2} + \frac{2AP}{B^2}\Big)\frac{x}{1+Bx} - \frac{1.734A}{(N-B)^2(1+Nx)}\\ &-\Big(\frac{1.734A}{(N-B)^2} + \frac{2\times 1.734AB}{(N-B)^3}\Big)2{,}3026\log\ (1+Nx)\Big]_{x_1}^{x_2}AB \qquad (18)\end{aligned}$$

By substituting $A' = 1.4476$, $B' = 0.0701$, $N = 2.2318$ and $P = 0.15266$, this reduces to the form

$$\begin{aligned}\Delta E = &+0.088731\Big[-4.35554x - 2\log\ x + 145.129\ \log\ (1+0.0701x) - \frac{0.802146}{1+2.2318x}\\ &- 0.059896\ \log\ (1+2.2318x)\Big]_{x_1}^{x_2}AA + 0.088731\Big[+89.9424x - 5907.46\\ &\log\ (1+0.0701x) + \frac{91.2374x}{1+0.0701x} - \frac{0.537147}{1+2.2318x} - 1.31704\log(1+2.2318x)\Big]_{x_1}^{x_2}\Delta B \qquad (19)\end{aligned}$$

By using the values of AE from Column 5 of Table V and solving the resulting deviation equations by the method of least squares, it was found that $AA = +0.00240$ and $AB = +0.00125$. Hence $A'' = 1.4476 + 0.00240 \doteq 1.4500$ and $B'' = 0.07010 + 0.00125 = 0.07135$. Then, using these second approximations for A and B, the values for $E_2 - E_1$ were recomputed by means of Equation 15, with the results shown in Table V. The corresponding deviations are shown in Col. 7. The average deviation, disregarding the sign, is only 0.09 millivolt. The only deviations exceeding 0.1 millivolt are for the 0.005 and 0.001 molal solutions and these solutions are so dilute that the measurements are not so reliable as for the more concentrated solutions, as will be apparent from Table II. Moreover, the deviations are about equally positive and negative, so that the sum, including the sign, is only -0.00004 volt. This equation was plotted in Fig. 1, Line II. The deviations being now within the experimental error, there is nothing to be gained by further computations by the method of successive approximations. Therefore our data on the electromotive force of barium chloride concentration cells with liquid junction and Lucasse's data on concentration cells without liquid junction lead to the conclusion that the transference number of the barium ion in barium chloride solutions at 25° is

$$t = \frac{1.4500}{1 + 0.07135\sqrt{c}} - 1 \qquad (20)$$

The hyperbolic form of the function $(t + 1)(\sqrt{c} + 1/B) = A/B$, which was found to be in accord with our data by the analytical method, is confirmed by the electromotive-force method and extended down to $c = 0.001$. The values of the transference number obtained by the electromotive-force method agree with those obtained by the analytical method to within 0.0024 throughout the entire range of concentration up to 1.0 molal. However, we believe that the results obtained by the analytical method are the more accurate.

In an exactly analogous manner the calculations were carried out with Lucasse's data on cells with transference and the results are shown in Table VI. The first deviations computed with $A' = 1.4476$ and $B' = 0.07010$ (based on the analytical data) are substantially greater than the corresponding deviations in our work and are predominantly positive. Then by the method described above it was computed that $AA = -0.0104$, and $AB = -0.01601$; hence $A'' = 1.4476 - 0.0104 = 1.4372$, and $B'' = 0.07010 - 0.01601 = 0.05409$. In these calculations the values for cells in which c is greater than 1 were not used because Hiickel's formula for the activity does not hold above 1 molal. Line III in Fig. 1 gives the corresponding plot of this equation.

The values for $E_2 - E_1$ computed with these values of A and B are shown in Table VI. The deviations, although larger than in Table V, are no longer systematic and the plus and minus deviations offset each other so nearly that no significant improvement can be made by repeating the calculations by successive approximations. Lucasse's data lead to the conclusion that the transference number is given by the equation

$$t = \frac{1.4372}{1 + 0.05409\sqrt{c}} - 1 \tag{21}$$

Line III in Pig. 1 gives the plot showing our interpretation of Lucasse's data. Curve IV in this figure is drawn by using the values of the transference number computed by Lucasse from the same data that were used in drawing Line III. We believe that Lucasse's computations of transference numbers from his data are erroneous and that when his data are properly interpreted they support rather than contradict our new hyperbolic relationship between the transference number and the square root of the concentration.

Further experiments on other salts to test the generality of our new hyperbolic relationship are under way.

Grateful acknowledgment is made of a grant from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

1. Improvements have been made in the details of Washburn's analytical method for the determination of transference numbers of chlorides which make it more precise, especially with dilute solutions.

2. The transference number of the barium ion in barium chloride solutions has been measured by the analytical method at 25° at many different concentrations in the interval from 0.01 to 1.035 molal and found to vary from 0.4378 to 0.3514 over this range.

3. The results can be expressed within the limits of the experimental error by a hyperbolic equation between the transference number of the barium ion, t, and the square root of the concentration, $\sqrt{c}$, as follows: $(t + 1)(\sqrt{c} + 14.2655) = 20.6501$, or its equivalent form

$$t = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1$$

4. The limiting value of the transference number of the barium ion in barium chloride solutions at infinite dilution at 25° is 0.4476.

5. The mean activity coefficient of the ions of barium chloride solutions varies with the concentration in accordance with the equation

$$\log_{10} f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$$

This function has the form derived by Hiickel.

6. The computation of transference numbers from the electromotive force of concentration cells with and without liquid junction is discussed.

7. Measurements have been made on the electromotive force of

concentration cells with liquid junction containing barium chloride covering the range from 0.001 molal to 1.0 molal. These data when combined with Lucasse's data on concentration cells without liquid junction lead to the conclusion that

$$t = \frac{1.4450}{1 + 0.07135\sqrt{c}} - 1$$

Transference numbers computed by this formula agree with those obtained by the analytical method within 0.0024 over the entire range of concentration up to 1.0 molal.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE SYSTEMS: STRONTIUM OXIDE-PHOSPHORUS PENTOXIDE-WATER, AND BARIUM OXIDE-PHOSPHORUS PENTOXIDE-WATER AT 25° (ACID REGION)

BY HERMAN V. TARTAR AND JAMES R. LORAH[1]

RECEIVED NOVEMBER 7, 1928 PUBLISHED APRIL 5, 1929

No investigation of the systems $SrO-P_2O_5-H_2O$ and $BaO-P_2O_5-H_2O$ has been reported in the literature. Investigation of the closely related system $CaO-P_2O_5-H_2O$ has been made by Cameron and his co-workers[2] and by Bassett.[3] Fairhall[4] has studied the system $PbO-P_2O_5-H_2O$.

Each system is one of three components. By working at a constant temperature, such a system may be made univariant, in which case the existence of a single solid phase is indicated by a variation in the composition of the solution. The formation of a second solid phase produces an invariant system, the solution being constant. Analyses of the solid and liquid phases of a series of empirical mixtures which have been permitted to attain equilibrium afford the data necessary for defining the conditions under which the different compounds exist in solid form.

For this investigation only those conditions under which at least three phases—gas, solid and solution—exist in equilibrium were of interest and the isotherms at 25° were determined. The composition of the solid phases was found by extrapolation, using Schreinemaker's[6] residue method. Analyses were made of the saturated solution and of the solid residue together with the adhering mother liquor. The values from the two analyses when plotted on a coordinate system lie on straight line, which when projected passes through a point representing the composition of

---

[1] DuPont Fellow at the University of Washington, 1926–1927.

[2] (a) Cameron and Seidell, THIS JOURNAL, 27, 1503 (1905); (b) Cameron and Bell, *ibid.*, 27, 1512 (1905).

[3] (a) Bassett, *Z. anorg. chem.*, 59, 1 (1908); (b) *J. Chem. Soc.*, 111, 620 (1917).

[4] Fairhall, THIS JOURNAL, 46, 1593 (1924).

[5] Schreinemaker, *Z. physik. Chem.*, 11, 81 (1893).

the solid phase. Similar lines located by the analyses of different mixtures at equilibrium pass through a common point which represents the composition of the solid phase.

Owing to the fact that phosphoric acid is very soluble, while strontium and barium oxides are only sparingly so, the entire range of experiments cannot be carried out easily in the same way; adsorption by the solid phase in alkaline solution is another complicating factor. The acid region only is treated in this paper. Further information regarding the compounds which exist in the basic region is given in the paper which follows.

Experimental **Part**

1. Preparation of Materials.—All of the materials used in the preparation of various salts were high grade "C. P. Analyzed" chemicals. The sirupy phosphoric acid (85%) gave negative tests for hydrochloric and sulfuric acids, heavy metals and reducing substances. The water used was the "conductivity water" of the laboratory, specific conductance approximately 2×10^{-6} mhos.

The monophosphates of strontium and barium were prepared by dissolving the hydroxides with an excess of moderately concentrated phosphoric acid, evaporating until crystals began to appear on the surface of the solution and then cooling rapidly with stirring to produce small crystals. The density of these solutions was so great that it was found advisable to use some means of stirring during their evaporation. The crystals were filtered by suction and washed with alcohol and then with ether. The alcohol and ether employed were anhydrous to prevent hydrolysis of the salts. The salts contained no water of hydration and analyses gave the following values: monostrontium phosphate, 36.60% SrO, 50.13% P_2O_5, ratio P_2O_5/SrO, 1.370 (theoretical, 1.371); monobarium phosphate, 46.69% BaO, 42.65% P_2O_5; ratio, P_2O_5/BaO, 0.933 (theoretical, 0.926).

Distrontium phosphate was made by adding slowly to a solution of 50 cc. of sirupy phosphoric acid per liter of water, solid powdered strontium hydroxide until *a* small amount remained undissolved, meanwhile keeping the solution rapidly stirred. The solid material was removed by filtration. The filtrate was next slowly heated and rapidly stirred. At about 60° a very fine precipitate of distrontium phosphate began to form, due to the hydrolysis of the monostrontium phosphate in solution. The precipitation was nearly complete when 75° was reached. The precipitate was filtered by suction and washed with alcohol and ether.

A different procedure was necessary for the preparation of dibarium phosphate. To a solution containing approximately 50 g. of barium oxide and 60 cc. of sirupy phosphoric acid per liter, dilute carbonate-free ammonium hydroxide (5%) was added drop by drop, the solution being thoroughly stirred. The gelatinous particles of tribarium phosphate which formed when the drops of ammonium hydroxide came in contact with the solution rapidly dissolved when stirred. The dibarium phosphate separated in crystalline form. The acidity of the solution at the end of the precipitate varied from PH 5 to 6.5.

2. Methods **of** Analysis.—(a) Strontium.——The sample was dissolved in 25 to 50 cc. of distilled water with the addition of 1 to 2 cc. of concentrated hydrochloric acid. Then an amount of alcohol exactly equal to the combined volume of aqueous solution and dilute sulfuric acid (1:20) used as the precipitating agent was added. Next, 5 to 10 cc. of the sulfuric acid solution was run in drop by drop while the solution was stirred. After standing from six hours to overnight at 10°, the precipitate of strontium sulfate, which meanwhile became crystalline, was filtered in a Gooch crucible, washed with 50% alcohol and moderately ignited.

(b) Barium.—The determination of barium was made in the usual manner in the form of the sulfate.

(c) Phosphorus.—The phosphorus determination was made using the filtrate from the strontium and barium sulfate precipitations. The filtrates were boiled to expel alcohol and then evaporated to small volume. Often the filtrates were diluted to a given volume and an aliquot portion taken. The solution was made slightly acid, as shown by the indicator brom thymol blue. Then phosphorus was precipitated by the addition of magnesia mixture,[6] followed by slowly adding dilute ammonium hydroxide until the precipitate of magnesium ammonium phosphate had completely formed. After half an hour concentrated ammonium hydroxide was added to the extent of one-eighth the volume of the solution. After standing overnight the precipitate was separated by filtration and dissolved in hydrochloric acid. The phosphorus was then reprecipitated as magnesium ammonium phosphate, filtered and finally ignited to constant weight as magnesium pyrophosphate.

3. Experimental Procedure.—To aqueous solutions of phosphoric acid of varying concentration were added the solid phosphates, the solid mono- and diphosphates to saturation. This was done by adding one phosphate until the solution was almost saturated and then adding the other phosphate in small quantity; for example, if the monophosphate was first used a small quantity of the diphosphate was used to "seed" the solution. After "seeding," the bottles containing the solution were tightly stoppered and carefully sealed. The bottles were then placed either in an oven maintained at 35°, or placed directly in a thermostat maintained at 25 ± 0.03°. Final equilibrium was attained in all cases at the latter temperature.

Series A and C were made up with monostrontium phosphate, Series D with distrontium phosphate, Series E and F with monobarium phosphate and Series G with dibarium phosphate. Series C and E were kept at 35° for three weeks in order to saturate them at that temperature. The former (Series C) was then allowed to stand at 25° for five weeks with thrice daily shakings while the latter was shaken constantly for one week at the same temperature. None of the others was ever heated to a higher temperature, since they were more dilute in phosphoric acid and hydrolysis would probably occur at the higher temperatures. Series A, D, F and G were allowed to stand at 25° for three weeks with thrice daily shakings. A and F were then shaken constantly for two weeks and D and G for three weeks at this same temperature. At the end of the period of shaking the solid and liquid phases of all samples were analyzed.

To obtain the samples for analysis the bottle containing the desired solution was removed from the thermostat, quickly wiped dry, opened and about **25 cc.** of the solution filtered by suction into a small vial. In order to prevent evaporation by drawing air through the moist residue, the suction was turned off just as all of the liquid had passed through the filter. The Gooch crucible used in this filtration had a thin layer of asbestos on the bottom to keep any small crystals from going through. On top of this was a Witt plate to protect the thin asbestos mat and on top of all was a small disk of hardened filter paper. The solid could be easily removed from the filter paper without tearing or damaging it in any way. In very concentrated phosphoric acid solutions the paper was not used.

The clear filtrate was used for the density determination and for the sample for the analysis of the liquid phase. During the filtration and density determination, the room temperature was maintained near 25°. The entire wet solid was analyzed. The

---

[6] Employed the magnesia mixture recommended by Lundell and Hoffman, *J. Ind. Eng. Chem.*, **15, 44 (1923).**

evaporation of water from either the liquid or solid phases was almost entirely prevented by placing the samples in tared, stoppered weighing bottles immediately after filtration. All the samples were then weighed within the following ten minutes.

Duplicate determinations on separate weighed portions of the solution were made in almost all cases, while a single determination on the solid phase was deemed sufficient; in many cases there was not sufficient material for duplicate determinations. The results are given in tabular form in Tables I and II, and graphically in Figs. 1 and 2.

TABLE I

ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM $SrO-P_2O_5-H_2O$

	Liquid phase		Solid phase		
Expt.	Strontium as SrO, %	Phosphorus as P_2O_5, %	Strontium as SrO, %	Phosphorus as P_2O_5, %	Density of liquid phase
CA	0.05	61.97	24.91	53.90	1.687
CB	0.13	56.49	25.67	52.01	1.594
CC	0.44	51.07	25.62	50.55	1.527
CE	1.78	43.80	27.36	48.55	1.455
CF	3.24	38.73	24.90	46.33	1.418
CG	4.61	35.90	26.48	45.68	1.410
CH	6.52	31.65	26.77	45.22	1.394
CI	8.08	27.63	27.82	43.54	1.379
AA	8.42	25.92	28.17	43.23	1.360
AB	8.88	24.71	28.46	42.72	1.357
AC	9.25	23.58	(a)	(a)	1.351
AD	7.84	20.79	35.02	30.80	1.294
AE	7.52	19.81	32.22	29.38	1.278
AF	6.53	16.66	32.27	28.18	1.230
AG	6.32	13.41	37.65	29.22	1.194
DA	5.11	12.70	(b)	(b)	1.169
AH	4.13	7.80	50.89	35.68	1.112
AI	3.18	6.02	45.11	32.05	1.083
DB	2.67	5.68	(b)	(b)	1.074

(a) Insufficient for analysis, microscopic examination showed it to be monostrontium phosphate. (b) Insufficient for analysis; microscopic examination showed it to be distrontium phosphate.

TABLE II

ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM $BaO-P_2O_5-H_2O$

	Liquid phase		Solid phase		
Expt.	Barium as BaO, %	Phosphorus as P_2O_5, %	Barium as BaO, %	Phosphorus as P_2O_5, %	Density of liquid phase
EB	0.85	53.79	38.43	43.28	1.580
EC	1.02	52.61	37.17	43.54	1.561
ED	1.50	49.22	37.17	42.69	1.524
EE	2.72	44.34	37.77	42.03	1.483
EG	6.93	33.74	39.26	40.65	1.425
FA	7.41	32.68	35.68	39.88	1.420
EH	9.14	28.36	37.09	38.81	1.397
EI	10.86	23.46	36.79	36.93	1.354
FB	8.50	16.15	51.46	26.70	1.246

Table II *(Concluded)*

	Liquid phase		Solid phase		
Expt.	Barium as BaO, %	Phosphorus as P_2O_5, %	Barium as BaO, %	Phosphorus as P_2O_5, %	Density of liquid phase
FC	6.84	12.35	Lost	Lost	1.188
GA	6.09	11.36	50.18	25.16	1.166
FD	6.31	11.19	59.46	28.82	1.165
FE	4.80	8 25	Lost	Lost	1.118
GB	4.33	7.61	37.90	20.08	1.107
FF	3.66	5.95	52.38	24.93	1.085
GC	2.00	2.96	37.44	18.49	1.040

Fig. 1, representing the system $SrO–P_2O_5–H_2O$, shows two stable phases, distrontium phosphate, Sr_2HPO_4, and monostrontium phosphate, $SrH_4(PO_4)_2$. The region in which the former is stable is bounded by A B C, and the latter by C D E. The area A C E represents the region which is not saturated and where no solid phase can be in equilibrium. Any region above the area A B C D E represents a state of supersaturation. At the point C, approximately, the two solid phases are in equilibrium with the solution. It is unfortunate that in experiment A C (Table I)

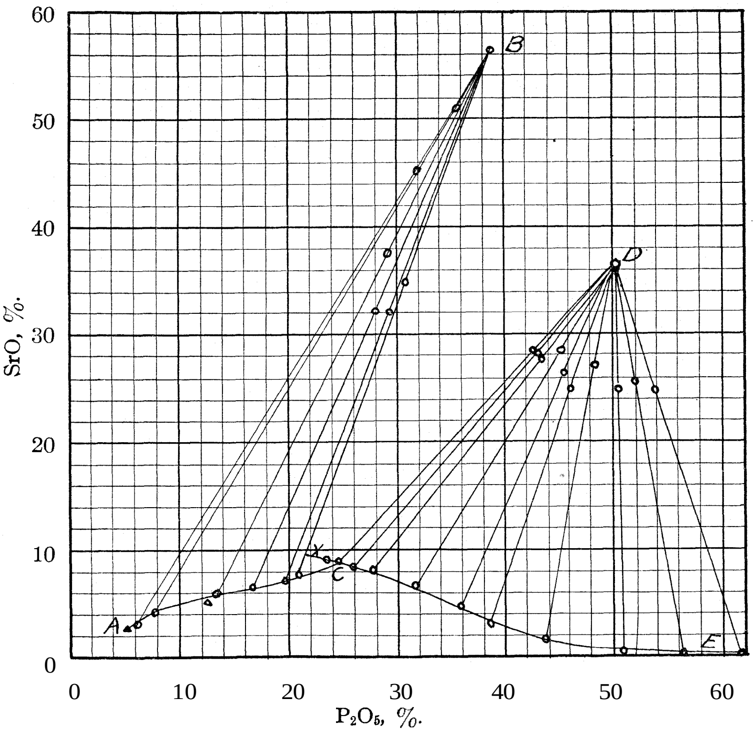


Fig. 1.—The system $SrO–P_2O_5–H_2O$.

the solid phase was too small for analysis; these data would show more conclusively the exact location of the invariant point. The extension C X probably represents a state of supersaturation with respect to distrontium phosphate as the solid phase. The lines A C and C E may be regarded as the solubility curves of di- and monostrontium phosphate, respectively, with respect to solutions of varying content of phosphoric anhydride.

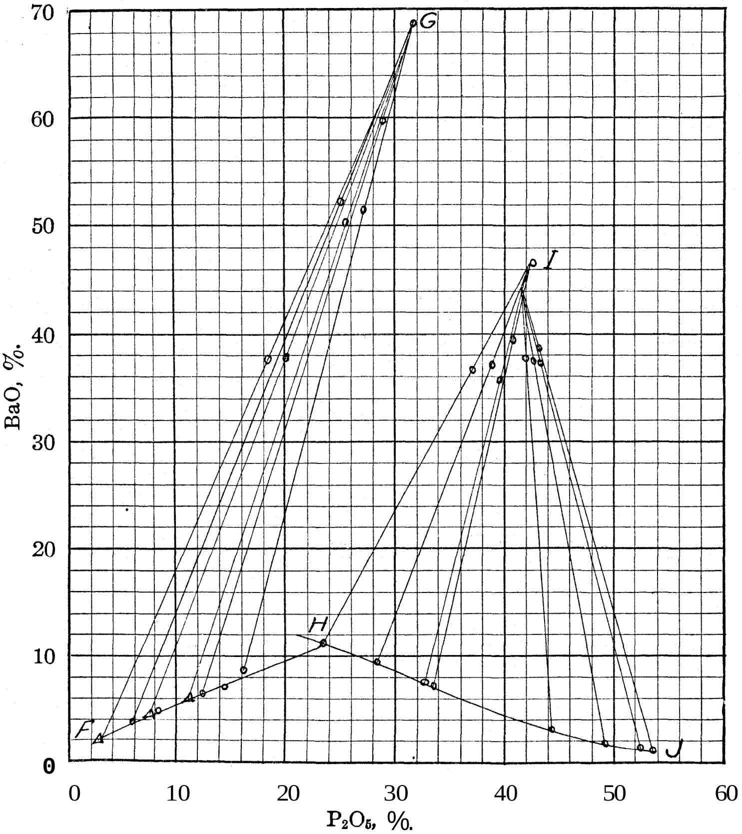


Fig. 2.—The system $BaO-P_2O_5-H_2O$.

The system $BaO-P_2O_5-H_2O$, represented in Fig. 2, is very similar to the $SrO-P_2O_5-H_2O$ system. Within the range of acidity of the system studied there are two stable solid phases. These are anhydrous di- and monobarium phosphates, represented by points B and I. The line FH represents the solution in stable equilibrium with dibarium phosphate and the line H J the stable equilibrium with monobarium phosphate. The point represented by H is the solution which can be in stable equilibrium with both di- and monobarium phosphates.

Summary

1. A phase rule study has been made of the system $SrO-P_2O_5-H_2O$ in the acid region. The limits at 25° have been defined for the two solid phases, monostrontium phosphate and distrontium phosphate.

2. A similar study has been made of the system $BaO-P_2O_5-H_2O$, in which the limits are defined for the solid phases, monobarium phosphate and dibarium phosphate.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OR WASHINGTON]

A BASIC PIPOSPHATE OF CALCIUM AND OF STRONTIUM AND THE ADSORPTION OF CALCIUM HYDROXIDE BY BASIC CALCIUM PHOSPHATE AND BY TRICALCIUM PHOSPHATE

BY JAMES R. LORAH,[1] HERMAN V. TARTAR AND LILLIAN WOOD[2]

RECEIVED NOVEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The purpose of this research was to clarify somewhat the confusion regarding the existence of phosphates of calcium more basic than the tertiary phosphate, $Ca_3(PO_4)_2$. To make the investigation more comprehensive the existence of basic phosphates of barium and of strontium was included.

Basic phosphates of calcium, strontium and barium have been mentioned frequently in the literature but apparently they have never been prepared in pure form.

Blarez[3] reported analyses of basic phosphates of calcium, strontium and barium which showed an excess varying from one-third to one-half molecule of the oxide over that required for the tertiary phosphates. Bertholet and Longuinine[4] had previously obtained similar results for barium phosphate.

Warington[5] found that when tricalcium phosphate is boiled with water the solution becomes distinctly acid. He made a series of experiments by boiling tricalcium phosphate with water for varying lengths of time, twenty-four to fifty hours, the water being renewed at frequent intervals. His analytical results do not show a final solid phase of constant composition; he concluded that the formula $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ "is the one which agrees best with the analyses." He further states, "We have, however, no certain ground for concluding that the action of boiling

---

[1] DuPont Fellow at the University of Washington, 1926–1927.

[2] Miss Wood completed in 1920 a limited portion of the experimental work reported in this paper, v&., Expts. 1a, 2a, 4a and 5a (Table I) in which the basic calcium phosphate was obtained.

[3] Blarez, Compt. rend., 103, 264 (1886).

[4] Bertholet and Longuinine, *Ann. chim. phys.*, [5] **9, 33** (1876).

[5] Warington, J. *Chem. Soc.,* **19,** 296 (1866); 26, 983 (1873).

water finally results in the formation of such a hydrated oxygen apatite, since we do not know what the further prolonged action of boiling water might effect."

Cameron and Seidell[6] noted in the precipitation of tricalcium phosphate that "when the supernatant liquid was alkaline, however, the precipitate always contained a larger proportion of lime than is required by the formula for tricalcium phosphate." Cameron and Bell[7] prepared a series of mixtures by adding lime water or dicalcium phosphate to phosphoric acid, which were agitated for three months at 25°. They obtained a series of solid phases which gave ratios, P_2O_5/CaO, varying from that of dicalcium phosphate to one much below that secured by Warington. They postulated a series of solid solutions intermediate between dicalcium phosphate and calcium hydroxide.

The solid solution explanation of Cameron and his co-workers has been criticized by Bassett,[8] who performed a series of experiments in which he shook mixtures of calcium oxide, dicalcium phosphate and water for eighteen months at 25°. He points out the serious experimental difficulties involved and states, "There seems little doubt that in spite of the length of time allowed, equilibrium had not been maintained in many cases." In one range he obtained solid phases with ratios, P_2O_5/CaO, varying from 0.881 to 0.831, which approximate "to the 0.845 for tricalcium phosphate, and it seems legitimate to conclude that in the main these solids do actually consist of this compound." In another group he obtained solid phases with ratios ranging from 0.798 to 0.763 "which are not far removed from the 0.761 of oxyapatite $(Ca_3P_2O_8)_3 \cdot CaO$, of which they appear to consist." With an excess of calcium hydroxide Bassett reports a solid phase with a ratio as low as 0.549.

Kolthoff,[9] from his results on the titration of phosphoric acid with calcium hydroxide using phenolphthalein indicator, was of the opinion that he had obtained a quaternary compound.

Jolibois[10] claims that from certain mixtures of calcium hydroxide and phosphoric acid he quickly obtained a new crystalline phosphate, $P_2O_5 \cdot 2CaO{-}P_2O_5 \cdot 3CaO{-}10H_2O$. In a later paper Jolibois and Maze-Sencier[11] have shown that calcium hydroxide is very strongly adsorbed by tricalcium phosphate when the latter is precipitated in the presence of the former. Hayashi and Matsui[12] report that the amount of calcium hydroxide required for the complete precipitation of the phosphate ion

---

[6] Cameron and Seidell, THIS JOURNAL, 27, 1503 (1905).

[7] Cameron and Bell, *ibid.*, 27, 1512 (1905).

[8] Bassett, J. *Chem. Soc.*, 111, 620 (1917).

[9] Kolthoff, *Chem. Weekblad*, 12, 662 (1915).

[10] Jolibois, *Compt. rend.*, 169, 1161 (1919).

[11] Jolibois and Maze-Sencier, *ibid.*, 181, 36 (1925).

[12] Hayashi and Matsui, J. *Soc. Chem. Ind. (Japan)*, 29, 175 (1925).

from an alkaline sodium phosphate solution greatly exceeds the theoretical requirement for the formation of tricalcium phosphate.

Experimental Part

1. Preparation of **Materials.**—Tricalcium phosphate, $Ca_3(PO_4)_2$, was prepared from monocalcium phosphate, $CaH_4(PO_4)_2 \cdot H_2O$, which was produceci in a manner precisely analogous to that given in the preceding paper for monostrontium phosphate. Twenty grams of the monocalcium phosphate was dissolved in four liters of water and then carbonate-free ammonium hydroxide was added with constant stirring until the solution was distinctly alkaline. The amorphous, gelatinous precipitate was washed with water by decantation, allowing several hours between washings for the precipitate to settle. The washing was continued until the phosphate-ion content of the water had decreased to a minimum. The small amount of phosphate ion in the wash water came from two sources: (1) the solubility of the tricalcium phosphate and (2) the slow hydrolysis of the tricalcium phosphate, which will be discussed later.

Tricalcium phosphate "has an inherent slowness of precipitation."[13] When sufficient ammonium hydroxide for complete precipitation was added at once, the solution was quite alkaline and a small amount of basic calcium phosphate was formed. Practically it was found desirable to add the ammonium hydroxide at such a rate that the solution never became more than faintly alkaline. Theoretically the hydrogen ion should not be allowed to decrease beyond the point at which the tricalcium and basic calcium phosphates are in equilibrium. Although this point is not definitely known, it is on the acid side of neutrality. Consequently, the tricalcium phosphate prepared by the method given above contained a small amount of basic calcium phosphate. Analysis of a dried sample gave the ratio P_2O_5/CaO, 0.835 (theoretical for tricalcium phosphate, 0.845).

Tristrontium phosphate was prepared by a method analogous to that employed for the preparation of tricalcium phosphate. A portion of the moist material was washed with alcohol, then with ether and dried at 80°. Analysis gave the ratio P_2O_5/SrO, 0.458 (theoretical 0.457) and showed 4.75% of moisture (calculated by difference).

A different procedure was required for the preparation of tribarium phosphate. When a moderate excess of ammonium hydroxide was added to a dilute solution of monobarium phosphate, the precipitate was a mixture of dibarium phosphate and tribarium phosphate, the former being present in much greater quantity. By adding drop by drop a very dilute solution of barium chloride to a boiling, dilute solution of sodium phosphate, Na_2HPO_4, which was made strongly alkaline with carbonate-free sodium hydroxide, a precipitate of tribarium phosphate was obtained. Analysis gave the ratio P_2O_5/BaO, 0.295 (theoretical, 0.309).

2. Analytical Methods.—Strontium and barium and most of the phosphorus determinations were made by the methods given in the preceding paper. A portion of the phosphorus determinations was made in the usual way; the sample was dissolved in nitric acid, the phosphorus precipitated with ammonium molybdate, this precipitate was dissolved

---

[13] Holt, La Mer and Chown, J. *Biol. Chem.*, 64, 509 (1925).

in ammonium hydroxide and the phosphorus precipitated twice as magnesium ammonium phosphate, ignited and weighed as the pyrophosphate.

Two methods were used for the estimation of calcium. A limited number of the determinations was made by precipitating with ammonium oxalate from a solution of the sample made slightly acid with acetic acid; then dilute ammonium hydroxide was added until the solution was only faintly acid, as shown by the indicator bromothymol blue. After standing hot for one hour the precipitate was filtered and titrated with standard potassium permanganate in the usual manner. This procedure is not quite as accurate as the usual one in which the precipitate is formed in ammoniacal solution; calcium oxalate is slightly more soluble in the acid solution.

The greater part of the calcium determinations was carried out by precipitating the calcium as sulfate. The sample was dissolved in 15 cc. of water, 2 cc. of concentrated hydrochloric acid and an amount of 95% alcohol equal to four times the volume of the aqueous solution were then added; finally, dilute (1:20) sulfuric acid was added drop by drop with constant stirring. After standing at 10° overnight, the calcium sulfate was filtered in a Gooch crucible, washed with 70% alcohol and gently ignited.

3. Hydrolysis Experiments.—A series of experiments was made treating the tertiary phosphates of calcium, strontium and barium with boiling water and with carbonate-free sodium hydroxide solution. A separate batch of phosphate was prepared for each experiment, which was carried out as follows. Approximately 10 g. of the moist phosphate which had not been dried was suspended in 4 liters of distilled water contained in a 5-liter Pyrex flask connected to a reflux condenser, the inner tube of which was also Pyrex glass. When hydroxide was present in the aqueous phase, the system was protected from the carbon dioxide of the air by a soda lime tube. The contents of the flask were boiled for eight hours each day. Every morning the supernatant liquid was carefully siphoned off and fresh water or solution added. At intervals a sample of the solid phase for analysis was removed with a pipet. The sample was washed with water and sometimes finally with alcohol and ether. The results of the hydrolysis experiments are reported in Table I.

All the samples were tested for the presence of carbonate with negative results.

The final product obtained from the hydrolysis of calcium phosphate gave a composition corresponding within experimental error to the compound $3Ca_3(PO_4)_2{\cdot}Ca(OH)_2$, for which the ratio P_2O_5/CaO is 0.760. The hydrolysis may be represented by the summary equation

$$10Ca_3(PO_4)_2 + 6H_2O = 3Ca_3(PO_4)_2{\cdot}Ca(OH)_2 + 2H_3PO_4$$

The basic phosphate is very insoluble and the reaction proceeds to a definite hydrogen-ion concentration when equilibrium is reached. If

TABLE I

RESULTS FROM THE HYDROLYSES OF THE TERTIARY PHOSPHATES OF CALCIUM, STRONTIUM AND BARIUM

Expt.	Boiling period, days	P_2O_5/MeO	Liquid phase for hydrolysis
	Tricalcium Phosphate		
1a	0	0.835	......
	25	.763	Water
	46	.752	Water
2a	25	.752	Water
	46	.762	Water
4a	28	.763	Water
5a	26	.764	Water
1	36	.770	Water
4	27	.775	Water
5	28	.765	Water
7	28	.765	Water
8	27	.753	Water
8	60	.760	Water
21	8	.772	0.05 M NaOH
21	22	.761	0.05 M NaOH
3	9	.746	0.5 M NaOH

Expt.	Boiling period, days	P_2O_5/MeO	Liquid phase for hydrolysis
	Tristrontium Phosphate		
32	0	0.458	.....
32	46	.439	Water
31	0	.458	......
31	8	.427	0.05 M NaOH
31	22	.422	0.05 M NaOH
31	45	.420	0.05 M NaOH
	Tribarium Phosphate		
11	0	.436	......
11	41	.422	Water
12	0	.329	0.05 M NaOH
12	20	.319	0.05 M NaOH

the acidic solution is removed by renewing the liquid in contact with the solid phase or by neutralizing the acid with alkali, the reaction proceeds to completion. After the solid phase reaches a composition giving the ratio P_2O_5/CaO, 0.76, it undergoes no change with further treatment.

The hydrolysis of the tristrontium phosphate took place more slowly than with the calcium salt. With water alone the conversion to the basic phosphate was very slow, only about half complete after forty-six days. In approximately half this time the material treated with dilute sodium hydroxide gave a solid phase corresponding in composition to the compound $3Sr_3(PO_4)_2\cdot Sr(OH)_2$ (theoretical P_2O_5/CaO ratio, 0.411). No change occurred upon further treatment with the sodium hydroxide.

Tribarium phosphate was difficult to prepare and the samples used for the hydrolysis experiments contained considerable amounts of dibarium phosphate; approximately two-thirds of the sample treated with water and one-half of the sample treated with alkali. With water only the hydrolysis of the diphosphate was exceedingly slow; with sodium hydroxide it was slightly more rapid. Even after twenty days' treatment with the alkali the ratio P_2O_5/BaO was 0.319, indicating that not all of the material was converted to the tertiary phosphate.

4. Precipitation from Alkaline Phosphate Solutions.—A series of experiments was made to prepare basic phosphates of calcium, strontium and barium by precipitation in alkaline phosphate solutions.

Ten grams of purified calcium carbonate was dissolved in dilute hydrochloric acid and the solution evaporated to dryness to remove the excess of acid. The residue was taken up in 2 liters of water. This solution was slowly added from a pipet to a boiling solution of 23 g of disodium phosphate (hydrate) and 95 cc. of saturated, carbonate-free sodium hydroxide solution in 2 liters of water. After standing overnight, the precipitate was washed with water until the wash water was practically free from chlorides. This required at least five washings with 3 liters of water each time, the solution being boiled for one hour to break up the large masses of precipitate, which was very gelatinous. Analysis of the dried precipitate gave the ratio P_2O_5/CaO, 0.781. Apparently the material was a mixture, largely the basic phosphate with some tricalcium phosphate.

The preparation of basic strontium phosphate was tried in a similar manner. A solution of 284 cc. of saturated strontium hydroxide (approximately 2.7 g. of $Sr(OH)_2$) was slowly added to a constantly stirred solution of 7.9 g. of disodium phosphate and 25 cc. of carbonate-free sodium hydroxide in 2 liters of boiling water. The flocculent precipitate was washed in the same manner as the calcium phosphate. Analysis gave the ratio, P_2O_5/SrO, 0 420, showing within experimental error that the material was the basic phosphate $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$ (ratio, 0.411). The precipitate was then boiled for ten days longer with water (3 liters each day); after this treatment, analysis gave the ratio, P_2O_5/SrO, 0.423.

On adding drop by drop a very dilute solution of barium chloride to a dilute solution of disodium phosphate strongly alkaline with sodium hydroxide, a precipitate was obtained which gave the ratio, P_2O_5/BaO, 0.295, showing the material to be tribarium phosphate (theoretical ratio, 0.309). In all of the experiments no evidence has been secured of the existence of a basic barium phosphate.

5. Absorption Experiments.—In order to ascertain whether there is a reaction between the basic calcium phosphate reported above and calcium hydroxide or whether the basic substances often mentioned in the literature were materials produced by adsorption phenomena, some experiments were made on the adsorption of calcium hydroxide by the basic salt and by tricalcium phosphate. Two adsorption isotherms were determined for the basic salt, one after three days' and the other after six months' standing, and one isotherm for the tertiary phosphate after sixteen hours' standing.

(a) With **Basic** Calcium Phosphate.—Each experiment of the series was carried out in the following manner. The desired amount of recently boiled distilled water was placed in a dry, well-paraffined Pyrex bottle. To this was added two 25-cc. portions of a suspension of the basic calcium phosphate, the suspension being first thoroughly mixed by pouring from one flask to another. The use of a 25-cc. pipet twice, instead of a 50-cc. pipet once, reduced the error which might be due to any settling of the suspended material. The basic phosphate was prepared by the hydrolysis of tricalcium phosphate with water; ratio, P_2O_5/CaO, 0.765. The calcium hydroxide solution was then measured from a buret attached directly to the bottle, the system being carefully protected from the carbon dioxide of the air. The stopper of the bottle was then sealed carefully with paraffin. About 10 cc. of air space was left in the bottle so that the contents could be shaken. The bottle was then kept at 25 ± 0.03" and frequently shaken.

A blank was prepared in the same manner except that distilled water was substituted for the basic phosphate suspension.

The analysis of the basic phosphate suspension was made by determining the calcium and phosphorus in a weighed portion. From these data the weights of the basic calcium phosphate and of water in the suspension were calculated.

The concentration of the calcium hydroxide solution was determined by titration with carefully standardized hydrochloric acid with phenolphthalein indicator; the same acid was used for all the titrations. To determine the calcium hydroxide in the solution after adsorption, the bottle was allowed to stand for a day to allow the solid phase to settle. The seal was then broken and a 100-cc. portion of the solution rapidly removed and titrated. The blank was titrated in precisely the same manner. The data from the experiments with the basic phosphate are presented in Table II and in Figs. 1 and 2.

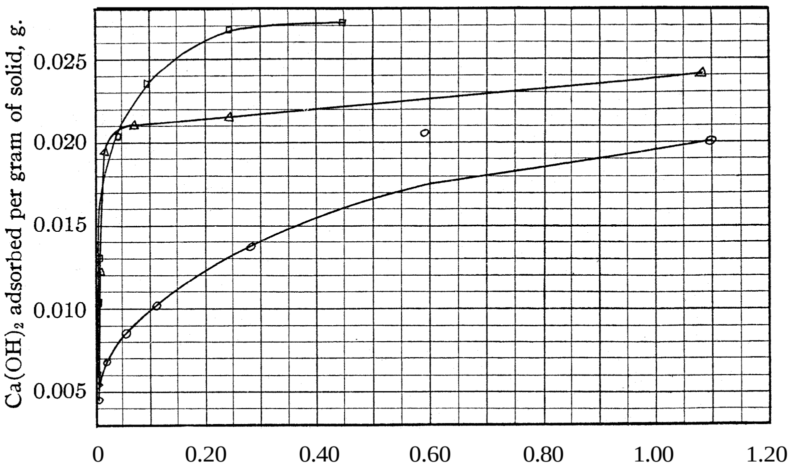
TABLE II

ADSORPTION OF CALCIUM HYDROXIDE BY BASIC CALCIUM PHOSPHATE AT 25°

0.8614 g. of basic calcium phosphate present in each bottle

Bottle number	Init concn. of $Ca(OH)_2$, g./l.	Final concn. of $Ca(OH)_2$, g /l.	Total vol. of soln., cc.	$Ca(OH)_2$ adsorbed per g. of solid, g.
		After Three Days' Standing		
25	1.176	1.099	224.69	0.0201
24	0.6706	0.5910	224.69	.0207
23	.3335	.2805	224.69	.0138
21	.1514	.1130	224.69	.0100
15	.0907	.0579	224.69	.0085
10	.0470	.0207	224.69	.0069
1	.0205	.0029	221.69	.0045
		After Six Months' Standing		
7	1.1760	1.0827	224.69	.0243
8	0.6706	0.5392	224.69	.0343
5	.3335	.2403	224.69	.0217
4	.1563	.0727	217.69	.0211
3	.0954	.0169	213.69	.0195
2	.0470	.0004	224.69	.0122
8	.0210	.0000	216.69	.0053

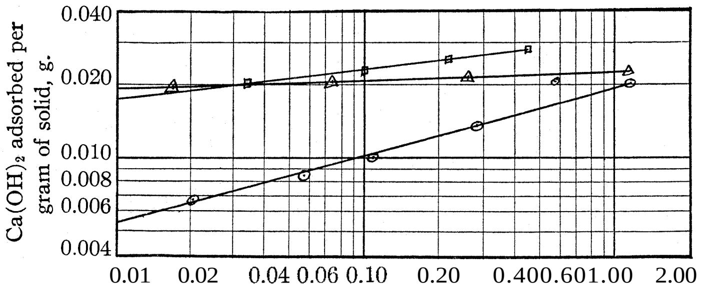
The curves from the two series of experiments (Fig. 1) are similar to the usual adsorption curve. When plotted logarithmically (Fig. 2), nearly straight lines are obtained, thus showing that the data may be represented by the common adsorption isotherm formulation proposed by Freundlich. There is no evidence of a reaction between basic calcium phosphate and calcium hydroxide. The two curves show that much more calcium hydroxide was taken up by the solid phase upon six months' standing. Usually adsorption equilibria are reached quickly and one might expect that if adsorption only took place there would be no further change after three days' contact. The change after this period may be due to the slow penetration of the calcium hydroxide into the interstices of the colloidal basic calcium phosphate. The writers are inclined to the opinion, however, that besides adsorption solid solutions were produced.



$Ca(OH)_2$ per liter after adsorption, g.

□, Tricalcium phosphate; △, six-month basic calcium phosphate; O, three-day basic calcium phosphate.

Fig. 1.—Adsorption of calcium hydroxide by calcium hydroxide.



$Ca(OH)_2$ per liter after adsorption, g.

□, Tsicalcium phosphate; A, six-month basic calcium phosphate; O, three-day basic calcium phosphate.

Fig. 2.—Adsorption of calcium hydroxide by calcium phosphates.

The data confirm the varying ratios obtained by Bassett[S] and by Cameron and Bell,[7] and apparently corroborate for this region the solid solution explanation proposed by the latter investigators.

(b) With Tricalcium Phosphate.—The series of experiments with tricalcium phosphate was run in precisely the same manner as that with the basic phosphate except that the contact between the solid and calcium hydroxide was limited to sixteen hours to minimize the change due to the slow reaction between these substances to form the basic phosphate. The tricalcium phosphate was prepared in the manner previously described. The results are reported in Table III and in Pigs. 1 and 2.

TABLE III

ADSORPTION OF CALCIUM HYDROXIDE BY TRICALCIUM PHOSPHATE AT 25° AFTER SIXTEEN HOURS

0.3838 *g.* of tricalcium phosphate present in each bottle

Bottle number	Init. concn. of $Ca(OH)_2$, g /l.	Final concn. of $Ca(OH)_2$,	Total volume of soln., cc.	$Ca(OH)_2$ adsorbed per g. of solid, g.
24	0.4990	0.4525	224.69	0.0272
23	.2848	.2388	224.69	.0269
15	.1390	.0989	212.69	.0234
10	.0699	.0348	224.69	.0205
1	.0278	.0043	224.69	.0131
47	.0188	.0011	224.69	.0103
48	.0110	.0002	224.69	.0064

The curves (Figs. 1 and 2) show that the data may be represented by the common adsorption isotherm formulation. The strong adsorption of calcium hydroxide by tricalcium phosphate affords at least a partial explanation of some of the basic materials which have been reported in the literature. Further experiments would be required to show whether solid solutions are possible in the range between tricalcium phosphate and the basic calcium phosphate.

Summary

1. The final product of the hydrolysis of tricalcium phosphate by water is a basic phosphate, the calcium and phosphorus contents of which correspond to that of the compound $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$. This compound is similar to the mineral apatite, the calcium fluoride or chloride of the latter being replaced by calcium hydroxide.

2. The point of equilibrium between tricalcium phosphate and basic calcium phosphate lies on the acid side of neutrality.

3. Tristrontium phosphate boiled with an aqueous solution of sodium hydroxide hydrolyzes to form a basic strontium phosphate, $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$, analogous to the basic calcium phosphate.

4. The hydrolysis of tricalcium and of tristrontium phosphate proceeds more rapidly with a sodium hydroxide solution than with water.

5. The basic strontium phosphate may be prepared by direct precipitation from an alkaline phosphate solution.

6. A method has been given for the preparation of tribarium phosphate.

7. No evidence has been obtained to indicate the existence of a barium phosphate more basic than tribarium phosphate.

8. The isotherm for the adsorption of calcium hydroxide shows that in most concentrated solutions approximately one-third of a mol of calcium hydroxide was adsorbed per mol of basic phosphate. Comparison of the curves for the three days' and six months' period indicates that either the calcium hydroxide penetrates the interstices of the solid phase very slowly or solid solutions are formed.

9. The adsorption of calcium hydroxide by tricalcium phosphate is slightly greater than by the basic phosphate.

10. The strong adsorption of calcium hydroxide by tricalcium phosphate and by basic calcium phosphate affords a basis for an explanation of many statements in the literature regarding basic phosphates of calcium.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VERMONT]

THE EQUILIBRIUM IN AQUEOUS SOLUTION BETWEEN AMMONIUM ACETATE, ACETAMIDE AND WATER

BY EDGAR E. LINEKEN AND GEORGE H. BURROWS

RECEIVED NOVEMBER 7, 1928 PUBLISHED APRIL 5, 1929

Introduction

The general reaction between ammonium salts of organic acids, the corresponding amides and water, though complicated by ionization and hydrolysis phenomena, in many instances runs smoothly and is adapted to studies in equilibria. In particular, it permits a comparison in equilibria among members of a homologous series.

E. E. Reid[1] has measured the benzamide formed upon heating until establishment of equilibrium of solutions of ammonium benzoate. Menschutkin[2] has studied the formation of amides on heating in closed glass tubes the pure ammonium salts of acids from formic to caproic, and also of benzoic and anisic acids. Other studies have been made purely from the standpoint of amide preparation.

E. A. Brodie, in this Laboratory, has measured the equilibrium between ammonium acetate and acetamide in aqueous solutions of several concentrations and at two temperatures. He heated the solutions to be brought to equilibrium in sealed pyrex glass tubes and analyzed the equilibrium mixtures through determination of their refractive indices. The present experiments are essentially repetitions of those of Brodie, substituting, however, for index of refraction, electrical conductance, thus lessening errors of analysis.

---

[1] Reid, *Am. Chem.* **J., 44, 76 (1910).**

[2] Menschutkin, **J.** ***prakt.*** *Chem.,* **[2] 29, 422, 436,** (1884).

Experimental

The acetamide used was twice crystallized from benzene, with centrifugal draining, and was dried at 50–70°, yielding odorless crystals.

The ammonium acetate was crystallized from absolute alcohol, centrifuged. washed with absolute ether, or alcohol, and dried for several hours at 40° in an atmosphere of dry ammonia gas. The crystals were kept in well-filled, tightly stoppered bottles.

Conductivity water of uniform quality was used in preparing all solutions. In the work of Mr. Brodie equilibrium was approached from both sides, and shown to be attained within two days, at 184 and at 193°. In most of the present experiments equilibrium was approached from the amide side only, this substance being less subject to change during weighing.

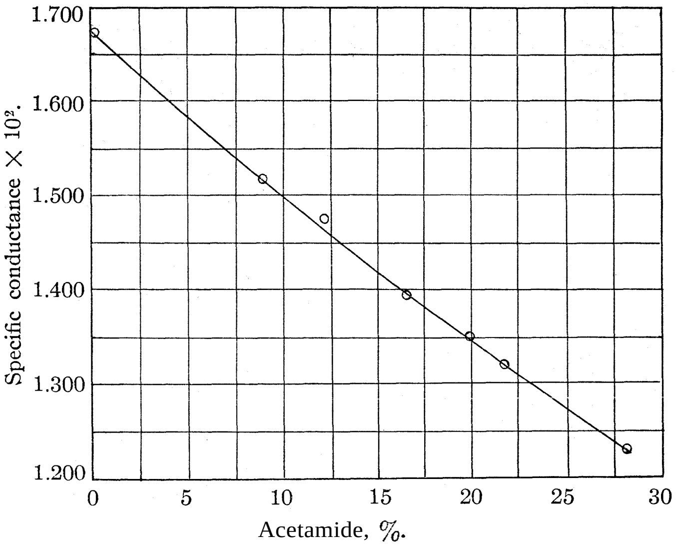


Fig. 1.

To attain equilibrium, solutions of acetamide were sealed in pyrex glass tubes of 5–10-cc. content, so that when hot the tubes would be closely full, and were heated in vapor-baths of dimethylaniline (193°), aniline (184") or secondary butylbenzene (172°), for the necessary length of time. After this they were plunged into cold water, opened and the contents of each tube, if not already of this concentration, were brought to a concentration of 0.2 mole of total solids (amide plus acetate) to 1000 g. of solution. Analysis was then effected by measuring the specific conductance of the solution and referring this to a curve (Fig. 1) plotted from conductance measurements on synthetic mixtures. The plot permitted reading to the nearest 0.1% of amide.

The data for the curve plotted are given in Table I. In this table the specific conductances are those of a series of synthetic solutions of ammonium acetate and acetamide, each of which holds the same total solute concentration of 0.2 mole of acetate plus amide to 1000 g. of solution.

TABLE I

DATA FOR CURVE

Solute as amide, %	28.35	21.99	20.00	16.92	12.32	10.51	9.16	0.00
Specific cond. $\times 10^2$	1.227	1.318	1.346	1.392	1.473	1.494	1.514	1.670

The results of the analysis of the equilibrium mixtures studied are given in Table II. They are shown graphically in Fig. 2

TABLE II

RESULTS OF ANALYSES

Tube	Concn. (moles amide + acetate in 1000 g. soln.)	Temp., °C.	Time of heating, days	Spec cond. at 0.2 *M* concn.	Total solute in form of amide, %
14	0.5	172	5	1.527×10^{-2}	8.4
15	0.5	172	5	1.521×10^{-2}	8.7
6	1	172	5	1.474×10^{-2}	11.6
7	1	172	6	1.474×10^{-2}	11.6
18	2	172	5	1.356×10^{-2}	19.3
19	2	172	5	1.356×10^{-2}	19.3
10	0.5	184	2	1.514×10^{-2}	9.2
11	0.5	184	2	1.514×10^{-2}	9.2
4	1	184	2	1.441×10^{-2}	13.8
5	1	184	2	1.437×10^{-2}	14.0
1	2	184	2	1.305×10^{-2}	
2	2	184	2	1.319×10^{-2}	21.9
3	2	184	2	1.319×10^{-2}	21.9
16	0.5	193	2	1.470×10^{-2}	11.9
17	0.5	193	2	1.467×10^{-2}	12.1
8	1	193	2	1.407×10^{-2}	15.9
9	1	193	2	1.407×10^{-2}	15.9
12	2	193	2	1.289×10^{-2}	24.0
13	2	193	2	1.289×10^{-2}	24.0

Identity in composition of Tubes 6 and 7 indicates that equilibrium was established within about five days at 172°, a temperature not used by Mr. Brodie.

For comparison, part of the data obtained by Mr. Brodie, through use of the refractometer as a means of analysis, are quoted. He determined the percentage of amide and of ammonium acetate at equilibrium by comparing the refractive index of the mixture with those of pure amide and pure acetate solutions of the same concentration. A refractive index–concentration curve for acetamide solutions and for ammonium acetate solutions, each plotted in the same coordinate frame, gave two converging and almost straight lines. The value for any mixture, of

TABLE III

DATA FOR PURE SOLUTIONS

Amide		Acetate	
Moles in 1000 g of soln.	n_D^{25}	Moles in 1000 g of soln	n_D^{25}
0.0000	1 33260	0 2700	1.33567
0.5000	1.33590	i.0147	i.34396
1.0000	1.33929	1.1242	1.34538
1.9924	1.34589	1,9924	1.35482
2.4410	1.34880	2.3102	1.35828
		2.6956	1.36270
		0.0000	1.33260

course, lay between these lines. The data for the pure solutions, and the curves plotted from these, are given in Table III and Pig. 3, respectively.

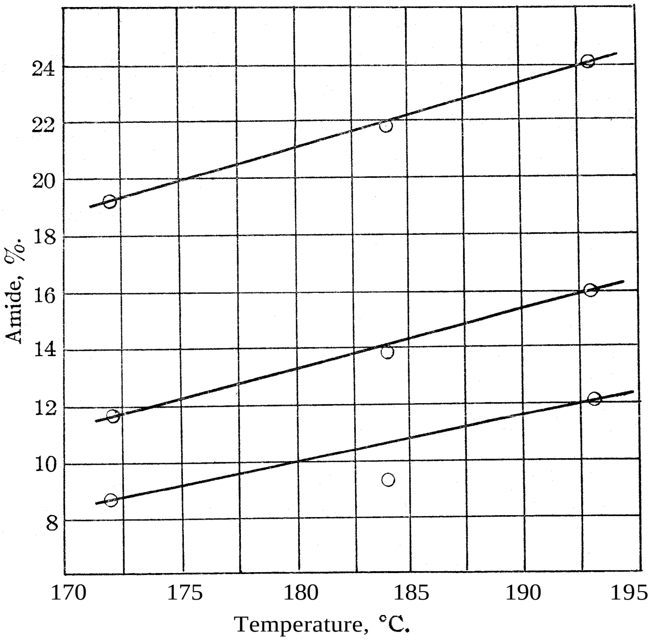


Fig. 2.

A summary of Mr. Brodie's analyses of equilibrium mixtures is given in Table IV.

TABLE IV

SUMMARY OF ANALYSES

Concn., moles solute/1000 g. soln.	2	2	1
Temperature, °C.	184	193	184
Soln. in form of amide, %	19.7	24.9	11.7

Approached from opposite sides, solutions of the same total solute concentration and at the same temperature always gave, at equilibrium, identical refractive readings, giving confidence in the purity of the amide and acetate used, and in the absence of side products.

Full treatment of the system under consideration would involve a knowledge of the ionization and of the hydrolysis of ammonium acetate at the concentrations and temperatures used. A. A. Noyes and co-workers[3] have determined such data for ammonium acetate in less concentrated solutions, at highest, approximately 0.01 molar.

An attempt was made to measure the equilibrium at this lower concentration. This failed, the results being quite irregular. In this attempt, refinements were made in the method of attaining equilibrium that will be mentioned.

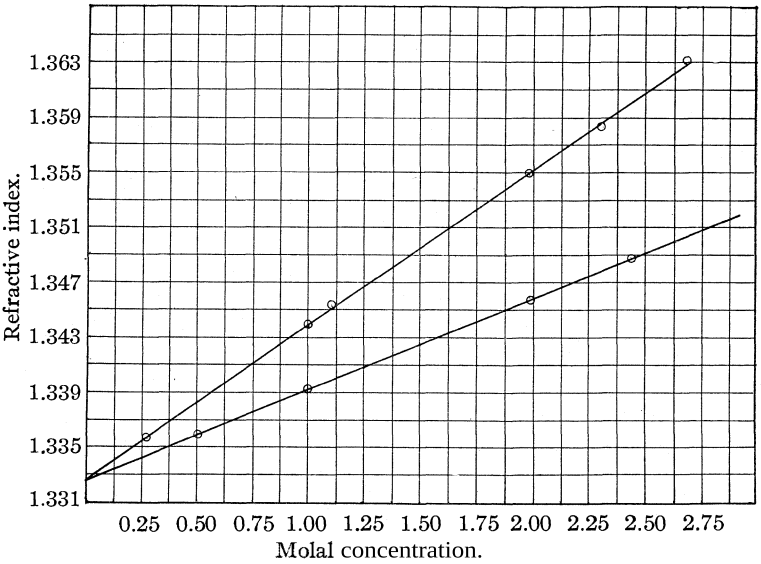


Fig. 3.

Though nothing of quantitative sort is known of the effect of the dissolved glass on the reaction itself, or of the effect of the reacting substances on the solubility of the glass, a brief study was made of the change

TABLE V

CHANGE IN CONDUCTANCE OF WATER WHEN HEATED IN PYREX GLASS

184°		193°	
Time	Incr. in spec. cond. × 10^{-5}	Time	Incr. in spec. cond. × 10^{-5}
1 Hour	2.101	1 Hour	3.632
5 Hours	1.50	4 Hours	3.58
4 Days	9.556	7 Hours	5.80
5 Days	7.758	5 Days	12.626

---

[3] A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," Carnegie Institute, 1907.

in conductivity of water when sealed in pyrex glass tubes of 5 to 10 cc. capacity and heated. The results are given in Table V.

The errors in the results due to this glass solubility at such concentrations as those recorded in Table II would be small, and likely within other errors of the method.

To minimize the effect of the solvent action on the glass, and that of the necessary residual gas space in the reaction tube, a different form of tube was designed, shown in Fig. 4. The glass tube A contains the loosely covered platinum cylindrical vessel D. The cover is kept in place by the platinum wire E. Tube A is connected to Tube B, and Tube B to Tube C by capillary tubing. The solution fills the apparatus to a suitable level in C, thus limiting to C any change in concentration due to evaporation into the gas space. The portion of the solution subjected to analysis is that contained in the platinum vessel. These precautions did not avail to give consistent results with solutions as dilute as 0.01 molar. A 2 molar solution of amide heated for two days at 184° in such a tube, then diluted to 0.2 molar, had at 25° a specific conductance of 13.36 X 10^{-4}, corresponding to 20.7% of amide remaining, and agreeing fairly well with the 21.9% of Table II.

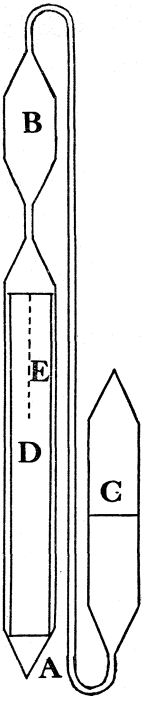


Fig. 4.

Examination of the data of Table II brings out that the ratios of the equilibrium concentrations of amide to those of ammonium acetate, including in the latter its dissociation and hydrolysis products, show, at a given temperature, no tendency to constancy. Such tendency is shown when the concentrations of amide are divided by the squares of the acetate concentrations (Table VI), indicating that the amide is formed through the interaction of the ammonium and the acetate ions.

TABLE VI

RELATIONS OF AMIDE AND ACETATE CONCENTRATIONS

Temp , °C.	Concn. of amide	Concn of acetate	$\frac{\text{Concn of amide}}{(\text{Concn. of acetate})^2}$
172	0.043	0.457	0.200
172	.116	.884	.148
172	.386	1.614	.148
184	.046	0.454	.2231
184	.139	.861	.1875
184	.438	1.562	.1795
193	.06	0.44	.31
193	.159	.841	.225
193	.48	1.52	.208

In Table VI the compositions are in moles per 1000 moles of solution.

Owing to the small concentration of amide, the first value for each temperature is the least accurate.

The conclusion that the amide is formed through the ions is in accord with such results as those of Walker and Hambly,[4] who show that the transformation of ammonium cyanate into urea is bimolecular

Summary

Results are given of measurements of the equilibrium between ammonium acetate, acetamide and water in aqueous solution at several temperatures and at several concentrations.

Evidence is presented that the amide is formed through the ions of the salt.

BURLINGTON, VERMONT

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

THE ACTIVITY COEFFICIENTS OF IONS IN VERY DILUTE METHYL ALCOHOL SOLUTIONS[1]

BY JOHN WARREN WILLIAMS[2]

RECEIVED NOVEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The fundamental equations of the activity theory of Debye and Hückel[3] have been amply verified in solutions in which pure water was used as the solvent. The validity of the fundamental equations with respect to the effect of the variation of the dielectric constant of the medium has not been sufficiently investigated, although it has been attempted in a number of cases.[4] For the work to be reported in this article the papers by Kraus and Seward[4e] and by Robinson[4f] are perhaps of greatest interest because they have used the same method to determine their activity coefficients and have used non-aqueous solvents. The purpose of these articles, as well as of the present one, is to attempt a verification of the

---

[4] Walker and Hambly, J. *Chem. Soc.*, ***67,*** 753 (1895).

[1] The work reported in this article was carried out during the months of November and December, 1927, under the direction of Professor J. N. Brönsted. At that time the work could not be continued and extended; therefore, it was withheld from publication In the meantime articles by Kraus and Seward and by Robinson, to which references will be made, have appeared which make it desirable to publish the results to date. The continuation and extension of the work has now been begun at the University of Wisconsin.

[2] National Research Council Fellow in Chemistry.

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

[4] ((a) Scatchard, THIS JOURNAL, ***47,*** 2098 (1925); (b) Noyes and Baxter, *ibid.*, ***47,*** 2122 (1925); (c) Nonhebel and Hartley, *Phil.* Mag., 50, 729 (1925); (d) Baxter, THIS JOURNAL, 48, 615 (1926); *(e)* Kraus and Seward, J. *Phys. Chem.*, **32,** 1294 (1928); (f) Robinson, *ihid.*, **32,** 1089 (1928); (g) Bronsted and Williams, THIS JOURNAL, 50, 1338 (1928).

manner in which the activity coefficient of the ions varies with the dielectric constant of the solvent in solvents whose dielectric constants differ from that of water by a considerable amount. According to the theory, it will be recalled that in a sufficiently dilute solution

$$-\log f_i = \frac{3}{2.3}\,\alpha z_i^2\sqrt{\mu}$$

and

$$-\log f_s = \frac{3}{2.3}\,\alpha z_1 z_2\sqrt{\mu}$$

where α is a constant depending only upon the dielectric constant of the solvent, D, the absolute temperature, T, and a numerical constant. The quantity f_i is the activity coefficient of an ion of the i^{th} sort, while f_s is the activity coefficient of the salt itself.

The activity coefficient of either ion or salt varies inversely with the product of the dielectric constant of the solvent by the absolute temperature, raised to the three-halves power.

$$-\log f \sim \frac{1}{(DT)^{3/2}}$$

Kraus and Seward conclude that their results are not at all in agreement with the interionic attraction theory. The activity coefficients were determined by means of the effect of solvent salts, sodium nitrate and ammonium nitrate, on the solubility of sodium chloride in *iso*-propyl alcohol, and by means of the effect of the solvent salt sodium nitrate on the solubility of sodium bromide in acetone. Kraus and Seward state, "The divergence of the experimental results from those required according to the interionic attraction theory bears no apparent relation to the dielectric constant. In order to bring the observed values in the more dilute solutions into conformity with the theory, it would be necessary to assume for the dielectric constant the value 5.3 for acetone with sodium bromide and sodium nitrate; 7.2 for isopropyl alcohol with sodium chloride and sodium nitrate, and 11.4 with sodium chloride and ammonium nitrate." Robinson, in studying the effect of four solvent salts of two valence types on the solubility of potassium bromide in acetone, finds that the observed solubilities are all greater than those demanded by the theory. The increases in solubility are, however, of the right order of magnitude to be expected from the Debye-Hückel theory, and Robinson suggests that traces of water in his acetone may account completely for the differences found. The dielectric constant of these solvents, acetone and isopropyl alcohol, is in the neighborhood of twenty.

The measurements to be reported in this article were made in pure methyl alcohol at 20°. Using the value 30 for the dielectric constant of the alcohol at this temperature,[4c] the equation for the activity coefficient of the salt, f,, becomes

$$-\log f_s = 2.02122\sqrt{\mu}$$

where z_1, z_2 = valence of the ions in question; μ = ionic strength. The more complete Debye-Hückel equation which takes into account an atomic diameter has not been used in the discussion to follow.

Experimental

The activity coefficients were determined by means of the effect of solvent salts of two valence types on the solubility of highly insoluble saturating salts, also of two valence types. An apparatus of the usual type for solubility work was used for the preparation of the saturated solutions. The following systems were studied: (I) solvent, methyl alcohol; saturating salt, croceo chloride; *solvent* salts, sodium benzenesulfonate, potassium sulfocyanate, barium chlorate, strontium benzoate;—(11) solvent, methyl alcohol; saturating salt, chloropentammine cobalt nitrate; solvents salts, potassium sulfocyanate, barium chlorate;—(III) *solvent*, methyl alcohol; saturating salt, xantho chloride; solvent salts, potassium sulfocyanate, barium chlorate, strontium benzoate.

The analyses were made by measuring a fixed quantity of the saturating solution, adding sufficient sodium hydroxide solution and distilling the ammonia liberated on boiling into a known quantity of standard acid through a quartz condenser tube. Brom cresol purple served as indicator in making the titrations.

The methyl alcohol used was purified by the method described by Bjerrum and Zechmeister.[5] The various complex cobalt ammine salts were prepared and purified according to directions given in the original works of Jorgensen and Werner. The various solvent salts used, with the exception of the strontium benzoate, were Kahlbaum chemicals of "C. P." grade. The strontium benzoate was specially prepared in this Laboratory. These solvent salts were tested for ammonia before use.

TABLE I

SOLUBILITY RELATIONS OF UNI-UNIVALENT SALT, CROCEO CHLORIDE, IN METHYL ALCOHOL AT 20°

Concn of salt, m/l.	No of detns.	Soly. X 10^4	μ	$\sqrt{\mu}$	log S/S_0
		1. Solvent Salt, $C_6H_5SO_2ONa$			
0.0000	7	6.020	0.000602	0.02450	0 0000
.0005	4	6.203	.001120	.03350	.0130
.0010	4	6.364	.001636	,04045	.0241
.0015	4	6 525	.002153	,04640	.0350
.0020	4	6.657	.002666	.05160	.0437
.0030	4	6 840	.003684	,06073	.0555
.0040	3	7 025	.004703	.06856	.0671
.0050	4	7.215	.005722	,07560	.0786
.0100	2	7.877	.010788	.10381	.1168

---

[5] Bjerrum and Zechmeister, *Ber.*, 56, 894 (1923).

TABLE I (*Concluded*)

Concn. of salt, m./l.	No of detns.	Soly. X 10^4	μ	$\sqrt{\mu}$	log S/S_0
		2. Solvent Salt, KSCN			
0 000	6	6 020	0 000602	0 02450	0.0000
.001	4	6.422	.001642	.04051	.0281
.002	4	6.685	.002669	.05167	.0455
.003	4	6.946	003695	,06080	.0621
.004	4	7.140	.004714	.06865	.0741
.005	4	7.355	.005736	,07573	.0870
.010	2	8 047	.010805	.10398	.1260
		3. Solvent Salt, $Ba(ClO_3)_2$			
0.00000	6	6.020	0 000602	0.02450	0.0000
.00025	2	6.550	.001405	.03748	.0366
.00050	2	6 810	,002181	.04670	.0536
.00100	2	7.275	,003728	,06105	.0822
		4. Solvent Salt, $Sr(C_6H_5COO)_2$			
0.000000	6	6.020	0.000602	0 02450	0.0000
.000125	2	6.163	000991	.03146	.0102
.000250	2	6.305	.001380	.03716	.0201
.000500	2	6.435	,002143	,04630	.0290
.001000	2	6.662	.003666	.06055	.0440

TABLE II

SOLUBILITY RELATIONS OF THE BI-UNIVALENT SALT, CHLORO-PENTAMMINE COBALT NITRATE, IN METHYL ALCOHOL AT 20°

Concn of salt, m /l.	No of detns.	Soly X 10^4	*a*	$\sqrt{\mu}$	log S/S_0
		1. Solvent Salt, KSCN			
0.0000	4	2.845	0.000854	0 02924	0.0000
.0005	2	3.110	.001433	.03785	.0387
.0010	2	3.323	.001997	.04470	.0675
.0020	2	3.727	.003118	.05584	.1173
		2. Solvent Salt, $Ba(ClO_3)_2$			
0.0000	4	2.845	0.000854	0.02924	0.0000
.0002	4	3.568	.001671	.04089	.0984
.0005	4	4.318	,002795	.05286	.1812
.0010	4	5 448	,004635	.06808	.2822
.0015	4	6.392	.006417	.08010	.3516
.0020	4	7.327	,008199	,09055	.4108

TABLE III

SOLUBILITY RELATIONS OF BI-UNIVALENT SALT, XANTHO CHLORIDE, IN METHYL ALCOHOL AT 20°

Concn. of salt, m./l.	No of detns.	Soly. X 10^4	μ	$\sqrt{\mu}$	log S/S_0
		1. Solvent Salt, KSCN			
0 00000	2	1.825	0.000548	0 02340	0.0000
,00025	2	1.894	.000819	,02862	.0162
.00050	2	1.966	.001090	.03302	.0324
.00100	2	2.134	,001639	.04047	.0680
.00200	2	2.424	.002727	.05235	.1233

TABLE III (Concluded)

Concn. of salt, m./l.	No. of detns.	Soly. X 10^4	μ	$\sqrt{\mu}$	log S/S_0
2. Solvent Salt, $Ba(ClO_3)_2$					
0.00000	2	1.825	0.000548	0.02340	0.0000
,00025	2	2.452	,001486	,03855	.1283
.00050	2	2.624	.002286	.04781	.1577
.00100	2	3.073	.003922	.06263	.2263
3. Solvent Salt, $Sr(C_6H_5COO)_2$					
0.00000	2	1.825	0.000548	0.02340	0.0000
.00025	2	2.274	.001431	.03798	.0956
.00050	2	2.529	,002259	.04751	.1417

Results

The solubility relations of the saturating salts in the various solvents are given in Tables I to III. The solubility is given in a great majority of the cases as either the average of two or four independent determinations, of which the individual values do not differ from their mean by more than 0.4 of 1% in any case. The concentrations in the tables are moles per liter.

Discussion

The values of the logarithm of the solubility ratio, log S/S_0, obtained directly from the analytical data have been plotted against the square roots of the ionic strengths and the limiting slopes of the resulting curves determined. In order to show the type of curves obtained, the data of Table I are represented graphically in Fig. 1.

The comparison of the limiting slopes obtained for the different systems with those predicted on the basis of the Debye-Hückel theory is interesting. These data have been collected to form Table IV.

TABLE IV

COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES

Saturating salt	Valence type	Solvent salt	Obsd lim. slope	Theor. slope	Agreement
Croceo chloride	1–1	$C_6H_5SO_2ONa$	1.7	2.0	Satisfactory
Croceo chloride	1–1	KSCN	1.7	2.0	Satisfactory
Croceo chloride	1–1	$Ba(ClO_3)_2$	2.5	2.0	Approximate
Croceo chloride	1–1	$Sr(C_6H_5COO)_2$	1.7	2.0	Satisfactory
Chloropentammine cobalt nitrate	2–1	KSCN	4 0	4.0	Satisfactory
Chloropentammine cobalt nitrate	2–1	$Ba(ClO_3)_2$	8	4.0	Very poor
Xantho chloride	2–1	KSCN	4.0	4.0	Satisfactory
Xantho chloride	2–1	$Ba(ClO_3)_2$	6	4.0	Poor
Xantho chloride	2–1	$Sr(C_6H_5COO)_2$	6	4.0	Poor

An inspection of the table shows that in sufficiently dilute solutions the limiting law of Debye and Hückel is obeyed. In the case of the simplest type salt, croceo chloride, the value observed for the slope in the case of three solvent salts, namely, 1.7, must be considered to be in satisfactory agreement with the theoretical slope, 2.0. It may be recalled that in water solution a salt of this type gives a slope of the order of magnitude 0.45 instead of 0.50 as demanded by the theory.[6] Thus a slope is found in methyl alcohol solution, which, as is the case in water solution, is from 10 to 15% lower than that demanded by the theory.

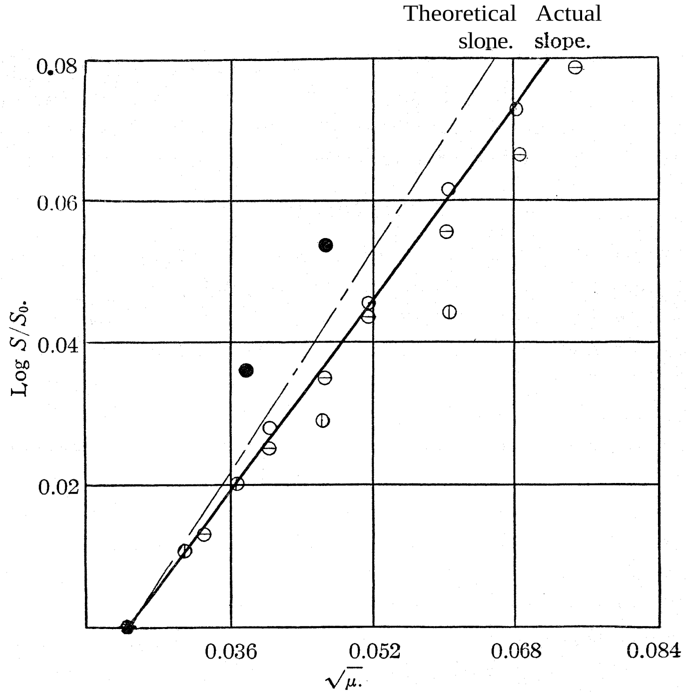


Fig. 1.—Solubility relations of uni-univalent salt croceo chloride in methyl alcohol at 20". Solvent salts: ○, KSCN; ⊖, $C_6H_5SO_2ONa$; ⦶, $Sr(C_6H_5COO)_2$; ●, $Ba(ClO_3)_2$.

The slope found when barium chlorate is used as solvent salt is considerably higher than that demanded by the theory, not only in the case of the 1–1 valence type salt but also in the case of both 2–1 valence type salts used. The explanation appears to be that either barium chlorate is not suitable for use as a solvent salt with any of the saturating salts used, or specific interactions of the ions interfere in the solubility effects produced. It may be mentioned that this substance was used as a solvent salt in less exact measurements on the solubility of the bi-univalent salt rhodanopentammine nitrate, and it was found that the resulting slope was of the order of magnitude 3 to 3.5, a value which is much more nearly that predicted by the theory. Rhodanopentammine nitrate is soluble

---

[6] Bronsted and Brumbaugh, THIS JOURNAL, 48, 2018 (1926).

only to the extent 0.00005 mole per liter and analyses could not, with the means available at the time of these experiments, be made with the same degree of accuracy as those for which results are given in the tables above. Therefore, the fact that slopes in closer agreement with the theory were not found when barium chlorate was used as solvent salt is not considered to be due to a failure of the theory.

In the case of salts of valence type 2–1, the theory is exactly obeyed when potassium sulfocyanate is used as solvent salt, but less exactly when strontium benzoate is used. However, it is probable that with salts of higher valence types, the theory will not be obeyed at concentrations of the order of magnitude reported in this communication.

Conclusions

The important fact indicated by the work which has been done to date is that if the solutions are made sufficiently dilute, the Debye and Hiickel theory will be obeyed in methyl alcohol solutions, at least for saturating salts of the simpler valence types. The range of applicability of the theory will probably depend upon the solute as well. It is not possible with the data available at the present time to discuss this point.

Further, it appears that as the dielectric constant of the solvent medium decreases, the highest concentration at which the simple activity theory will be obeyed also decreases. Thus in the case of a saturating salt of valence type 1–1, dissolved in water, and using a solvent salt of like type, the Debye-Hückel limiting law is obeyed to a total salt concentration of approximately 0.01 molal, but when suitable salts of the same valence types are dissolved in methyl alcohol, the limiting law is obeyed only to a total salt concentration of 0.002 molal. If acetone or isopropyl alcohol is used as a solvent, it would then be expected that an agreement with the theory could be obtained only if a total salt concentration of something less than 0.001 molal is used. It must be remembered, too, that the saturating salts which are suitable for the purpose under discussion must meet a number of criteria, not only as regards their own solubility but also in relation to the solvent salts which can be used with them.

These results indicate the importance of studying the interionic attraction theory in media whose dielectric constants are between that of water and of methyl alcohol. In this manner the limiting concentrations for which the theory will be obeyed for each of the different valence type salts will be ascertained. It is evident also that the study of the effect of various solvent salts on the solubility of a given saturating salt in the various media is of importance, particularly from the standpoint of the principle of the specific interaction of ions proposed by Brönsted.[7]

---

[7] Brönsted, THIS JOURNAL, 44, 877 (1922); 45, 2898 (1923); Güntelberg, *Z. physik. Chem.*, 123, 199 (1926).

The author takes this opportunity to thank Professor J. N. Bronsted for facilities placed at his disposal and for his constant advice and encouragement during the course of the work. It is also a pleasure to thank Mr. E. Güntelberg, also of this Laboratory, for discussions of the subject matter.

Summary

1. The activity coefficients of several slightly soluble complex cobalt-ammine salts of the simpler valence types have been determined in pure methyl alcohol by the solubility method. These data have been utilized to test the validity of the simple Debye and Hückel equations.

2. The important conclusion to be drawn is that in sufficiently dilute methyl alcohol solution and using saturating and solvent salts of the simpler valence types, the general ideal equations of Debye and Hückel are obeyed. It seems probable that the range of applicability of the theory will depend also upon the solute used.

COPENHAGEN, DENMARK
MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

DIFFERENTIAL POTENTIOMETRIC TITRATION. III. AN IMPROVED APPARATUS AND ITS APPLICATION TO PRECISION MEASUREMENTS

BY DUNCAN A. MACINNES AND MALCOLM DOLE

RECEIVED NOVEMBER 8, 1928 PUBLISHED APRIL 5, 1929

Introduction

Since the first paper on this subject by MacInnes and Jones[1] several articles have appeared[2] which contain criticisms of the method or offer suggestions as to changes in the apparatus. An objection to the original arrangement has been that the electrode and shield as used by MacInnes and Jones is complicated and difficult to construct. There are, we have found, additional disadvantages. In the first place, as originally designed

---

[1] (a) MacInnes and Jones, THIS JOURNAL, 48, 2831 (1926); (b) MacInnes, *Z. physik. Chem.*, (Cohen-Festband), 217 (1927).

[2] (a) W. A. Roth, *Z. Electrochem.*, 33, 127 (1927); (b) Rabinowitch and Kargin, *ibid.*, 34, 311 (1928); (c) Hall, Jensen and Baeckström, THIS JOURNAL, 50, 2217 (1928). In two recent papers Erich Muller [(d) *Z. physik. Chem.*, 135, 102 (1928); (e) *Z. angew. Chem.*, 41, 1153 (1928)] claims first publication of the idea of a retarded electrode and, by implication at least, of the method of differential titration. As evidence he refers to a paper [(f) *Z. Electrochem.*, 31, 323 (1928)] in which data on pairs of bimetallic titrations are given. In one of each pair one electrode was wrapped with asbestos, thus hindering diffusion. We consider Müller's claim to priority on this evidence as rather fantastic. The first differential titrations were performed by Cox, THIS JOURNAL, 47, 2138 (1925).

it is difficult to make a shield in which the retained solution will not be disturbed by vigorous stirring. Also quite a number of up and down movements of the cap shielding the retarded electrode are necessary, after a reading, to make sure that the concentration of the solution around the two electrodes is the same. This has the effect of slowing up a determination. A still more serious disadvantage is that the sheltered electrode is permanently attached to the apparatus with the result that it cannot be changed if "poisoned," or if it is necessary to change the type of electrode used.

The New Apparatus

In order to overcome these defects we have designed and tested the differential apparatus shown in Fig. 1. The retarded electrode E is surrounded by a tube A having a capillary outlet C at the bottom. Solution from the beaker is circulated over the electrode by means of a simple gas lift L operated by a stream of gas passing through the tube G. By stopping the gas stream the portion of the solution in the tube A is isolated from the bulk of the solution, and does not react when the titrating solution is added from the buret B. On restarting the gas stream the solution in A is soon mixed with that in the beaker and the composition of the solution in this tube is made uniform with the bulk of the solution. The construction of the gas lift pump is easily within the powers of the amateur glass blower. The small hole H prevents the solution from running over the top of Tube A in case the gas stream is too rapid. The capillary C may be quite fine, but should not be small enough to be readily clogged. An advantage of this arrangement is that the electrodes E and E′ can be of any convenient form, are not attached to the apparatus, and can be changed, even, if necessary, in the course of a titration. The two electrodes may be fastened together using a small separator, and can then be placed astraddle the tube A.

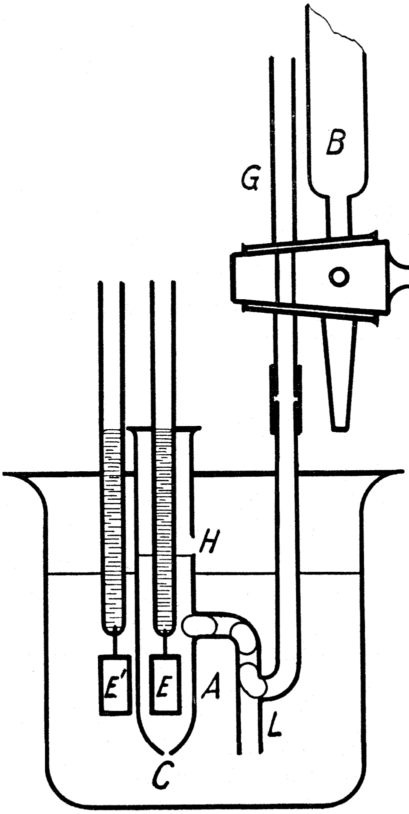


Fig. 1.

An additional convenience, but not altogether necessary for the operation of the apparatus, is the type of buret stopcock S as shown in Fig. 1. This stopcock is arranged so as to regulate the gas stream as well as the titration fluid. As shown the buret is closed and the flowing of the gas stream is producing circulation through the tube A. If, however, the stopcock is turned through a small angle the gas stream is turned off, thus isolating the solution in **A.** On turning still further the titrating fluid runs out of the buret. If the stopcock is turned back just enough to stop the flow of titrating fluid, the gas stream will not start and a reading of the potential between the electrodes E and E′ may be made. **A** short turn further causes the gas to flow again and renews the circulation.

Since this circulation soon produces uniformity in concentration throughout the apparatus the potential difference between the electrodes E and E′ should rapidly reach zero. If the electrodes are well adapted to the titration in hand this is found to be the case, except in the immediate region of the end of the titration where a short delay in attaining zero difference may be observed. We have found that observations of the speeds with which the zero is reached are of greatest use in determining the relative advantages for a particular titration of electrodes of different designs.

Titrations can be much more rapidly carried out if the operator does not have to set a potentiometer for each reading. The potential can be read directly in deflections of a galvanometer without polarizing the electrodes by means of one of the various forms of apparatus involving radio tubes. Arrangements for carrying out titrations in this manner have been described by Goode,[3] Treadwell[4] and others. A difficulty with most arrangements of this kind is that the zero is constantly shifting due to the sensitiveness of the radio tubes to slight changes in the current used for heating the filament. We have, however, found that the amplifier for ionization currents designed by Wynn-Williams[5] largely overcomes this difficulty and has far more than the necessary sensitivity for our measurements. Some measurements were also carried out with a potentiometer in the usual way.

The Combined Direct and Differential Procedure

An unexpected advantage of the apparatus shown in Fig. 1 is that the tube A can serve as a temporary reservoir for a small portion of the solution while a rough idea of the end-point is being obtained. To find this preliminary end-point the gas stream is stopped and the titrating solution is added until a large potential difference is found between the electrodes E and E′. This amounts to making a preliminary non-differential titration in the manner described by Müller.[2d] The potential during the titration, for instance, of an acid by a base follows a course like that shown by the dotted line O–x–a in Fig. 2. Now if the titration has not been carried too far beyond the point of inflection x of this curve and the solution has not become too basic it can be brought back to the acid side of the end-point by starting the gas stream. The material in the tube A will

---

[3] Goode, THIS JOURNAL, **44,** 26 (1922).

[4] Treadwell, *Helv, Chim. Acta,* **8,** 89 (1925).

[5] Wynn-Williams, *Proc. Camb. Phil. Soc., 23,* 811 (1927); *Phil. Mag.,* 6,325 (1928).

then mix with the bulk of the solution and the difference between the two electrodes will return to zero. The exact end-point can then be found by the differential method as described above. At the final end-point the potential goes through a sharp maximum, as shown by the typical curve b–c–d. This procedure unites the advantages of the direct and differential methods, since the great bulk of the solution can be added rapidly and the precision and convenience of the newer method are retained. Ordinary titrations carried out by this method take very little more time than titrations involving the usual indicators, the limiting factor being the rapidity with which the electrodes respond to changes in concentration.

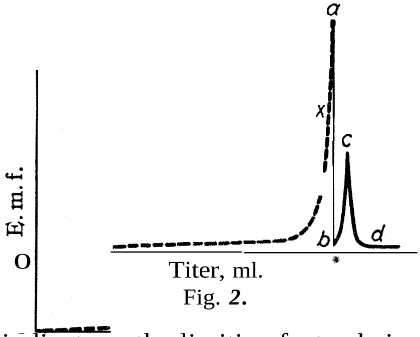
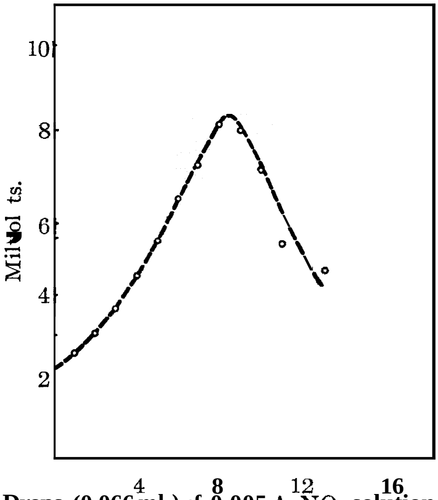


Fig. 2.

The Method Adapted to Precision Measurements

The main object of this investigation was, however, to continue the study commenced by MacInnes[1b] of the differential method as a means of making titrations of high precision. In such measurements the solution to be titrated was accurately weighed out into the beaker from a weight buret. With the gas stream stopped the titrating fluid was run from another weight buret until a point corresponding to a of Fig. 2 was attained. The titration was then continued by means of the differential procedure using, in the buret B of Fig. 1, the titrating fluid diluted in a known ratio, say 1 to 10 or 1 to 20. The success and accuracy of this procedure can best be judged by the results from the two different types of titrations outlined below.

The Titration of Ferrous Sulfate with Potassium Dichromate.—In a previous paper[1b] a failure was reported in the attempt to get accurate titrations of solutions containing ferrous ions, using the earlier differential technique, although the method yielded results of high accuracy for iodimetry and for the reaction between oxalic acid and potassium permanganate. The difficulty was probably due to an oxidation, catalyzed by the platinum electrodes, of the ferrous ions by atmospheric oxygen. We have, however, obtained excellent results by carrying out the titrations in an atmosphere of carbon dioxide. To this end a stream of that gas operated the lift pump and another stream bubbled through the solution to be titrated. A tall beaker was used in order to have a layer of the heavy gas between the solution and the air. The solution titrated was approximately 0.1 N ferrous ammonium sulfate. This was kept strongly acidified in an atmosphere of carbon dioxide during the measurements, and the volume of the solution drawn out of the container was replaced by that gas which was not, however, specially purified. The electrodes E and E′ were of smooth platinum gauze. Sixty to eighty grams of the acidified solution was weighed out into the beaker and 0.1 *N* potassium dichromate was added from a weight buret until the point a of Fig. 2 was obtained. The gas lift was then started and the titration continued with 0.01 N potassium dichromate, using increments of 0.1 cc., each of which corresponds to about 0.01%. However, the curve b–c–d is, in this case, extraordinarily sharp and definite, so that the true maximum could readily be interpolated to 0.002 or 0.004%. The data from a series of titrations are given in Table I, which is mostly self-explanatory. The figures in Col. 5 are the corrections to the weight of potassium dichromate solutions obtained from readings of the volumetric buret. The figures in Col. 6 show that there is a gradual increase in the ratio of the weight of the iron solution to the corrected weight of the dichromate solution. However, if these ratios are plotted against the times at which the individual titrations were carried out, a remarkably straight line is obtained. This result would follow if a slow oxidation of the ferrous sulfate solution occurred under the conditions of our experiments.



Drops (0.066 ml.) of 0.005 $AgNO_3$ solution.

Fig. 3.

TABLE I

TITRATION OF FERROUS SULFATE BY POTASSIUM DICHROMATE

Expt.	Time, hours	Weight of ferrous soln., g	Weight of $K_2Cr_2O_7$, g.	Corr. to wt. of (4)	Ratio, wt. $Fe/K_2Cr_2O_7$	Ratio at zero, time
1	0	86.064	76 284	0 067	1.12722	1.12722
2	26	62.070	54.694	.266	1.12937	1.12702
3	30	63.081	55 673	.115	1.12991	1.1271_9
4	31.5	66429	58.740	.048	1.12998	1.1271_2
5	122	60.500	53.115	.044	1.13810	1.1270_3
6	123.5	65.119	57.180	.031	1.13822	1.1270_2
7	126	76.718	67.331	.051	1.13855	1.12712

An idea of the accuracy of the measurements can be obtained by correcting all the ratios to zero time by means of the slope of the line just described. The ratios thus corrected, given in Col. 7 of the table, show a maximum variation of 0.02%. Apparently no rapid reaction with the oxygen of the air took place during a determination, as was found in the earlier experiments.

The Titration of Chloride Solutions with Silver Nitrate.—We have, however, been more interested in developing a rapid, convenient method for titrating chlorides as the necessity for this analysis occurs frequently in our work. Lange and Schwartz[6] describe, in a most excellent paper from which we have obtained many useful suggestions, a research in which they carried out direct electrometric titrations the results of which showed mean variations of only 0.003%. To get this precision required, however, elaborate precautions to prevent diffusion of chloride from the calomel half cell, and of the solution to be titrated into the salt bridge. They found it necessary to use an opposing flow of chloride-free ammonium nitrate solution to overcome the effects of these diffusions.

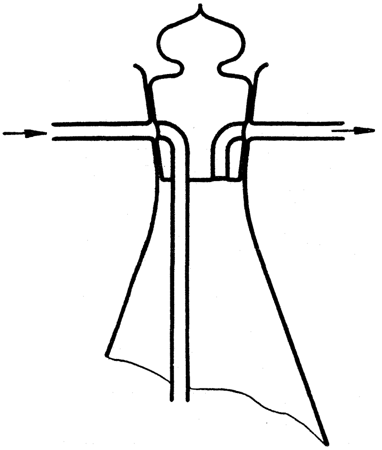


Fig. 4.

The procedure in our titrations followed that already described for the ferrous sulfate solutions with necessary changes to be outlined below. The solution to be titrated was an accurately prepared tenth (weight) normal potassium chloride solution made from the fused sodium-free salt. The titrating solution was approximately 0.1 N silver nitrate. The last part of the titrations was carried out with this solution diluted in the ratio 1 to 20. Following the suggestions of the authors just mentioned the titration was made with the beaker immersed in an ice-bath, and the solution in it was kept down to the smallest possible volume. Some of the electrodes used in this titration were made by coating a platinum wire with a paste of silver oxide and heating,[7] and with others the platinum was silver plated. The latter form of electrode is apparently the better for this purpose. To prevent slowing up of the electrode reaction due to an adherent coating of precipitated silver chloride, the upper part of the electrodes was given a vigorous tapping from the hammer of an electric bell. This tapping was also found necessary to keep the gas lift pump from clogging by the precipitated silver chloride. The entry tube of the solution to the gas lift was also given a slight constriction for the same reason. In these titrations a potentiometer was used instead of the Wynn-Williams bridge. A typical series of readings around an end-point are plotted in Fig. 3, indicating the magnitudes of the potentials and the definiteness of the curve.

---

[6] Lange and Schwartz, *Z.* Electrochem., 32, 240 (1926).

[7] Lewis, THIS JOURNAL, 28, 166 (1906).

The solutions were kept in two-liter Erlenmeyer flasks the necks of which were arranged as shown in Fig. 4. These flasks are particularly useful if it is desired to control the atmosphere above a solution. If the gas enters in the direction of the arrow it will bubble through the solution and eventually displace the air originally in the flask. To transfer the solution to another container the stopper is given a half turn. A flow of the gas in the same direction as before will then iorce the solution out of the flask. A quarter turn of the stopper will prevent the flow of either gas or solution. In the present work the air used to displace the solution was first bubbled through a solution of the same composition as that in the flask.

(a) The Titration of Potassium Chloride Solution.—The results of a series of titrations are given in Table II, with the ratios of the weights of the potassium chloride and silver nitrate solutions in the last column.

TABLE II

THE TITRATION OF 0.1 *N* POTASSIUM CHLORIDE WITH 0.1 *N* SILVER NITRATE

No.	Wt. KCl soln., g.	Wt. $AgNO_3$ soln , g.	Corr. to $AgNO_3$ soln.	Ratio $\frac{\text{wt. KCl soln.}}{\text{wt. AgNO}_3\text{ soln.}}$
1	38.858	39.441	0.030	0.98447
2	31.399	31.807	.088	.98445
3	39.875	40.359	.142	.98455
4a	25.589	25.970	.022	.98449
4b	25.639	25.970	.069	.98464
5	38.5304	39.0203	.1138	.98458

Of these determinations, that numbered 4b was made by adding more potassium chloride solution to the beaker and then going once more through the end-point, after the determination 4a had been made. Determination 5 was made with a separately prepared potassium chloride solution. The average of the last four figures was used in the computations which follow. The mean deviation (0.003%) is the same as that of Lange and Schwartz's measurements.

(b) The Analysis of Constant-Boiling Hydrochloric Acid.—Since we have, in this Laboratory, made much use of constant-boiling hydrochloric acid as a source of acid of known strength, it seemed desirable to determine whether the acid as we were preparing it had the strength assigned to it by the research of Foulk and Hollingsworth.[8] We have repeatedly proved the reproducibility of the concentration of successive distillations of the acid by means of conductance measurements. These showed that variations are not greater than 0.01%. The still, however, differs from that of the authors named in that it has a greater capacity (2 liters) and a larger condenser tube (1 cm. internal diameter). Also the rate of distillation was somewhat greater (7 cc. per min.) than they

---

[8] Foulk and Hollingsworth, THIS JOURNAL, 45, 1220 (1923).

used. The rate per unit of surface of acid is, however, within their recommended range.

Titrations of the middle fraction of the acid were carried out using the technique described in the last section, except that the acid had first to be neutralized. For this purpose a very nearly chloride-free alkali was prepared by recrystallizing sodium hydroxide twice from water. The resulting material, when neutralized, gave a barely perceptible turbidity with silver nitrate, certainly too little to affect the result. For analysis the constant-boiling acid was first diluted to 0.1 N and weighed portions of the dilute solution were titrated with the silver nitrate solution, standardization of which, against fused potassium chloride, is decribed in the previous section. The results of two titrations are given in Table III.

TABLE III

ANALYSIS OF CONSTANT-BOILING HYDROCHLORIC ACID

				% HCl	
No.	Wt. const.-boiling acid, g.	Wt. $AgNO_3$ soln., g.	Corr.	765.2 mm.	Corr. to 750 mm.
1	0.74385	41.8985	0.0823	20.2051	20.249
2	.71066	40.0368	.0676	20.2034	20.247
				Av.	20.248
				From Foulk and Hollingsworth	20.245

The column headed "weight of constant-boiling acid" is computed from the weight of the 0.1 N solution used by the accurately known factor of dilution. The last two columns contain the percentage of hydrogen chloride in the constant-boiling acid at 768 mm. and at 750 mm., the latter being obtained from the former by means of the factor (−0.0024%/mm.) used by Foulk and Hollingsworth. The usual corrections were applied to our barometer readings. The average of our determinations agrees remarkably closely with the value 20.245 given by those authors, whose measurements, however, ranged 0.004% above and below this. Foulk and Hollingsworth analyzed their solutions gravimetrically using the precautions, including the use of a nephelometer, developed at Harvard for atomic weight determinations. The outcome of this comparison of the gravimetric method with the differential potentiometric method is gratifying.

Conclusions and Comment

The differential potentiometric method using the improved apparatus has thus been shown to be suitable for rapid titrations of ordinary accuracy, and also for titrations of high precision. We feel sure that, using the technique already developed, still greater accuracy can readily be obtained.

Unless the counter-current method of Lange and Schwartz is used to overcome diffusion or convection of solution into the salt bridge, accuracy such as we have demonstrated cannot be obtained by the direct potentiometric method. Even with that device the solution is continually gaining in concentration of the solution used for the salt bridge. It is a desirable feature of the differential procedure that it introduces no extraneous material into the solution to be titrated. Another paper from this Laboratory will deal with the method as modified for the use of hydrogen electrodes.

From published comment[zb] it appears that there is uncertainty in the minds of some readers concerning the error involved in retaining a small proportion of the solution in the space around the retarded electrode, as, for instance, in Tube A of Fig. 1. A short consideration will show that the error E cannot be greater than

$$\frac{AT}{T} \times \frac{v}{V} > E$$

in which AT is the last increment of titrating solution, T is the total volume of this solution used and v and V are, respectively, the volume retained around the retarded electrode and the total volume. This is true because the final portion of titrating fluid reacts with all of the solution except a small proportion given by v/V. However, this small proportion of solution is only the fraction $\Delta T/T$ removed from the end-point. Thus if 50 ml. of solution are used with 0.1-ml. increments, and the tube A holds 4 ml. out of the 200 ml. in the beaker, the error will be

$$\frac{0.1}{50} \times \frac{4}{200} \times 100 = 0.004\%$$

Since such measurements are ordinarily made to one drop of solution, or about 0.1%, this error is negligible. In our work with weight burets the ratio $\Delta T/T$ is around 1/10,000 and the corresponding error is about 0.0002%, which is, of course, well within the experimental error.

Summary

An improved apparatus for differential potentiometric titration, involving a simple gas lift pump, is described. The usefulness of the method in analyses of high precision is shown in the titration of ferrous sulfate with potassium dichromate and of potassium chloride with silver nitrate. An analysis of constant-boiling hydrochloric acid, which agrees closely with the results of Foulk and Hollingsworth, has also been carried out.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. V. POTENTIOMETRIC STUDY OF THE REACTION BETWEEN FERROCYANIDE AND CERIC IONS

BY N. HOWELL FURMAN AND OLIVER M. EVANS

RECEIVED NOVEMBER 10, 1928 PUBLISHED APRIL 5, 1929

Introduction

In previous papers of this series[1] it has been shown that solutions of ceric sulfate, containing sulfuric acid, are suitable for use in volumetric analysis, especially with the aid of the potentiometric method of determining end-points. Independently of this series of studies, H. H. Willard and Philena Young[2] and I. A. Atanasiu[3] have studied some of the uses of ceric sulfate in volumetric analysis. H. Rathsberg[4] has recently employed the reagent in the determination of antimony and arsenic as did Willard and Young[2] and Furman and Wallace (unpublished).

In addition to the advantages of ceric sulfate that have already been pointed out by the investigators whom we have cited, *viz.*, (a) stability, (b) high normal oxidation–reduction potential, (c) simplicity of valence change as contrasted with the relations in case of permanganate, there is another that is of some interest: (d) ceric salts are almost unique among the stable powerful oxidizing agents in having a cation as the primary active constituent.[5] In most of the other cases, that is, permanganate, dichromate, chlorate, bromate, iodate, etc., the active constituent is an anion, or at least can only be liberated by the destruction of an anion. Owing to mutual attraction of oppositely charged ions, ceric salts might therefore be expected to be somewhat more effective, other things being equal, in the oxidation of anions than dichromate, or even permanganate. This appears to be true in the oxidation of nitrite, for example.

The Reaction between Ceric Sulfate and Ferrocyanide.—The reaction $Ce^{++++} + Fe(CN)_6^{----} \rightleftarrows Ce^{+++} + Fe(CN)_6^{---}$ proceeds quantitatively from left to right in acid solution and quantitatively from right to left in alkaline medium (30% potassium carbonate solution). Browning and Palmer[6] used the latter reaction as a basis for the volumetric de-

---

[1] N. H. Furman, THIS JOURNAL, 50, 755, 1675 (1928).

[2] Willard and Young, *ibid.*, 50, 1322, 1334, 1368, 1372, 1379 (1928); 51, 139, 149 (1929); Ind. Eng. *Chem.*, 20, 972 (1928).

[3] I. A. Atanasiu, *Bull. Soc. Roum. Chim.*, **30**, 1 (1927); Atanasiu and V. Stefanescu, *Ber.*, 61, 1343 (1928).

[4] Rathsberg, *ibid.*, 61, 1664 (1928).

[5] W. D. Treadwell (private communication) called attention to the possible importance of this factor.

[6] Browning and Palmer, *Am. J. Sci.*, 26, 83 (1908).

termination of cerium. Tomiček[7] has shown that the end-point may be determined potentiometrically.

Atanasiu and Stefanescu[3] have published data on but a single titration of ferrocyanide with ceric solution, and give no test analyses regarding the accuracy of the method. They state that the concentration of sulfuric acid does not alter the inflection in any way. We find that there is a fairly definite upper limit of acidity. We have also studied the reverse titration.

Experimental

The potentiometric titration apparatus did not differ in any essential respect from that which was used in the earlier investigations of this series. The indicator electrode was a bright platinum wire; the reference electrode, a normal calomel electrode.

The ceric solutions which were used in this investigation were prepared from commercial rare earth oxides[8] containing 45% of CeO_2 (44.94 and 45.24% of CeO_2 [bismuthate method)].

Prior to ignition the material dissolves readily and practically completely in dilute sulfuric or nitric acid. After ignition it is readily decomposed by heating with concentrated or dilute sulfuric acid (1 vol. acid of sp. gr. 1.84 : 1 vol. water). Over 90% of the available cerium is found to be present in the ceric condition in the resulting solutions. A solution approximately 1 N in sulfuric acid and others from 3–4 N in acid were prepared; the latter solutions were found to be stable, whereas the former decreased slowly in strength.[9]

The ceric sulfate was standardized potentiometrically against pure sodium oxalate. Addition of hydrochloric acid as suggested by Willard and Young[10] makes the potentiometric standardization convenient, whereas in sulfuric acid solution the standardization is accurate, although extremely tedious.[11]

[7] O. Tomiček, Rec. *trav. chim.*, 44, 410 (1925).

[8] We are indebted to Dr. H. S. Miner of the Welsbach Company, Gloucester, N. J., for this material, which is a commercial rare-earth oxide mixture that is available in quantity. The mixture usually contains about 55% per cent. of CeO_2 on a dry basis, the other oxides being chiefly those of lanthanum and neodymium, with smaller quantities of praseodymium and samarium oxides. We have found this to be the best available raw material for the preparation of ceric sulfate solutions. *Cf.* also Willard and Young, THIS JOURNAL, 51, 149 (1929).

[9] The decrease in strength is not due to reduction but to the gradual precipitation of ceric ion in part, at least, in the form of phosphate. The phosphate occurs in the crude rare-earth oxides and is brought into solution by the more concentrated acid which is first used to dissolve the oxide. Upon dilution a gradual separation of ceric salt begins and may continue for a week, or even longer, depending upon the conditions of acidity and dilution of the ceric salt.

[10] Willard and Young, THIS JOURNAL, 50, 1325 (1928).

[11] Furman, ibid., 50, 761 (1928).

Potassium permanganate solutions were standardized potentiometrically against the pure sodium oxalate.[12]

Approximately 0.1 or 0.05 *N* potassium ferrocyanide solutions were prepared. The content of the solution was checked at frequent intervals by potentiometric titration with the potassium permanganate.[13] The data thus obtained were used as a basis of judging the accuracy of the titration of ferrocyanide with ceric sulfate.

Titration of Perrocyanide with Ceric Sulfate.—The titrations were made at room temperature (20–25"). Appropriate quantities of the ferrocyanide solution and of acid and water were measured out. The rate of addition of ceric salt had little effect upon the accuracy of the titration. The results are summarized in Tables I and II.

TABLE I

TITRATION OF APPROXIMATELY 0 05 *N* FERROCYANIDE WITH 0.05 *N* CERIC SULFATE

	1	2	3	4	5	6
Initial acid concn , N	...	1.5	5 0	...	0.5	0.8
Ceric soln. found, cc.	25.30	2531	25.34	25.11	25.11	25.08
Ceric soln. calcd., cc.	25.32	25.32	25.32	25.09	25.09	2509
Error, cc.	−0.02	−0.01	+0.02	+0.02	+0.02	−0.01

The total initial volume was 100 cc.; in Nos. 2 and 3 the acid was hydrochloric, in 5 and 6, sulfuric.

Weighed portions of a dried specimen of "C. P." commercial potassium ferrocyanide required, respectively, 0.13, 0.17, 0.17, 0.14, 0.13 and 0.10% less than the calculated quantity of ceric sulphate. Unpurified potassium ferrocyanide would probably serve as a secondary standard in much the same way as does "C. P." Mohr's salt.

TABLE II

TITRATION OF 0.1002 N FERROCYANIDE WITH 0.1028 N CERIC SULFATE

A. In Hydrochloric Acid Solution

	1	2	3	4	5	6	7	8
Initial vol , cc.	100	100	60	100	100	60	60	100
Initial acid concn , *N*	0 9	0.9	...	0.6	0 9	1.0	2 0	0.6
Ceric soln. found, cc.	24.42	24.35	9.75	24.36	24.31	9 78	9.77	24.33
Ceric soln. calcd., cc.	24 37	24.37	9 75	24.37	24 37	9.75	9.75	24.37
Error, cc.	+0.05	−0.02	±0.00	−0.01	−0 06	+0 03	+0 02	−0.04

B. In Sulfuric Acid Solution

	1	2	3	4	5	6
Initial vol., cc.	60	60	60	60	60	60
Initial acid concn., N	1.0	1 5	3.0	1.0	2 0	3.0
Ceric soln. found, cc.	24 32	24.37	24.36	9.74	9.76	9.78
Ceric soln. calcd., cc.	24.37	24.37	24 37	9.75	9.75	9.75
Error, cc.	−0.05	±0.00	− 001	−0.01	+0.01	+0.03

---

[12] C. del Fresno, *Z. Elektrochem.*, 31, 199 (1925); S. Popoff and J. Whitman, THIS JOURNAL, 47,2259 (1925).

[13] E. Muller and H. Lauterbach, *Z.* anal. *Chem.*, 61, 398 (1922); I. M. Kolthoff, *Rec.* trav. *chim.*, 41, 343 (1922).

The general nature of the titration graph in the neighborhood of the end-point is indicated in Fig. 1. The character of the reverse titration is also indicated. The potential readings become steady almost at once except in the immediate region of the end-point, where the establishment of a steady potential reading requires one to three minutes, depending upon the conditions.

The concentration of acid should not be too high. With a ceric solution that is 1 N in sulfuric acid the initial concentration of sulfuric acid in the ferrocyanide solution should not exceed 5 N. If the initial acid concentration is too low, and if the acidity of the ceric solution is low, a white precipitate may be formed during the titration. With much more than 5 N original acid concentration, the end-point potential readings are established sluggishly, and some decomposition of the ferro- or ferricyanide may occur. With hydrochloric acid the results are excellent in the range 0.5–2 N. If the acid concentration is as high as 4 *N* at the end-point the rise in potential is not sharp.

The jump in potential at the end-point usually amounted to 0.15–0.25 volt per 0.05 cc. of 0.05 *N* solution, or 0.2–0.3 volt per 0.05 cc. of 0.1 N ceric solution.

The titration appears to be very accurate and much less circumscribed than the permanganate titration, where a very limited range of acidity is essential.

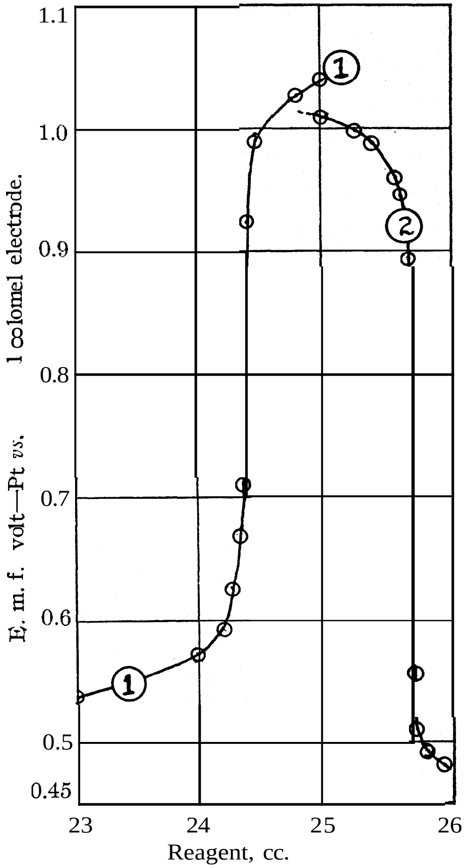


Fig. 1.—Curve 1, titration of 25 cc. of 0.1002 N ferrocyanide with 0.1027 N ceric sulfate. Initial volume, 60 cc. 1 N in sulfuric acid. Found, 24.36. Calcd., 24.37 cc. of ceric sulfate. Curve 2, the reverse of (1). Initial volume 75 cc., about 1 N in sulfuric acid. Calcd., 25.65 cc. Found, 25.66 cc. of ferrocyanide.

Visual End-Point.—During the titrations with ceric sulfate a greenish coloration is formed during the progress of the titration. This is apparently due to the formation of ferric ferrocyanide with a trace of iron that is found to be present in the ceric solution (thiocyanate reaction). Apparently the excess of ferrocyanide aids in keeping the ferric ferrocyanide in colloidal form.[14] The greenish coloration disappears quite sharply at the end-point when the last traces of ferrocyanide are oxidized.

It is possible to use the disappearance of the greenish color as a visual indication of the end-point. During the potentiometric studies the color end-point was observed to precede the potentiometric by 0.03, 0.00, 0.03, 0.00, 0.00, 0.04, 0.03 and 0.02 cc. The background was not very satisfactory for observation of the color change in these cases. A series of determinations was made by the visual method using a white tile background: found, 23.47, 23.48, 23.50, 23.49 cc. of approximately 0.1 N ceric solution per 25 cc. of ferrocyanide. Twenty-five cc. portions of the ferrocyanide were then titrated potentiometrically: found, 23.47, 23.47, 23.51, 23.49 cc. of ceric solution. The two methods are therefore in excellent agreement.

A portion of the ceric solution was treated with a slight excess of hydrogen peroxide and then boiled to decompose the latter. After appropriate dilution and withdrawal of an aliquot portion, the iron was estimated colorimetrically to be 1.00 ± 0.05 mg. per 25 cc. of ceric solution.

If a trace of ferric iron is added to a ferrocyanide solution that is being titrated with permanganate, the same greenish coloration forms and is destroyed in the same manner at the end-point.

Titration of Ceric Sulfate with Ferrocyanide.—This titration is only practicable under very limited conditions. The most important single factor is speed of titration. If the rate of titration is too small some ceric sulfate is apparently consumed by a side reaction, probably with ferricyanide, and too little ferrocyanide is used. For example, if the titration was interrupted after addition of 10 and 20 cc. of ferrocyanide, respectively, in order to take potential readings, only 25.53 cc. of ferrocyanide was required instead of 25.65 cc., the calculated quantity. The erratic nature of the results is indicated by the following figures, cc. of ferrocyanide (0.1002 N) found:

1	2	3	4	5	6	7	8	9
25.17	25.34	25.27	25.44	25.41	25.51	25.55	25.53	25.57

The amount theoretically required was 25.65 cc. in each case. In No. 1 the rate of addition was 5 cc. per minute. In instances 2–5 a relatively large number of interruptions was made for potential readings. In cases 6–9 only two readings were taken, one after rapid addition of 10 cc. and the other after 10 cc. more of ferrocyanide had been added. The titrations were then finished slowly. Under like conditions of operation the results are quite reproducible but seriously in error.

If from 80 to 97% of the theoretical amount of ferrocyanide is added very rapidly (fifteen to twenty-five seconds) the titration may be finished in the usual manner and the results are accurate, as is indicated in Table III.

---

[14] *Cf.* G. Rossi and M. Marzari, *C. A.*, 22, 1262 (1928).

TABLE III

TITRATION OF 0.1028 *N* CERIC SULFATE WITH 0.1002 *N* FERROCYANIDE

Initial vol., cc.	55	50	50	50	75	75	100	100
Ferrocyanide soln., cc.	25.60	25.60	25.65	25.67	25.66	25.68	25.63	25.65
Error, cc.	−0.05	−0.05	±0 00	+0.02	+0.01	+0.03	−0.02	±0.00

In each case 25.65 cc. of ferrocyanide should have been used The initial acid concentration ranged from 1 to 2.5 N. In the first instance 20 cc. of ferrocyanide was added, within about fifteen seconds, to the well-stirred ceric solution; in the other cases from 24.5–25 cc. was added rapidly before any potential readings were taken. The break in potential per 0.03 cc. of ferrocyanide at the end-point amounted to 0.23–0.34 volt. The readings were steady except in case of the drop that caused the large break in potential. Prom one to three minutes were required before the reading was steady. A drop of ferrocyanide in excess caused the appearance of the greenish coloration and was a reliable indication that the end-point had been passed. The general character of the potential curve is indicated in Fig. 1.

Summary

The potentiometric titration of ferrocyanide with ceric sulfate has been found to be accurate throughout a wide range of conditions and can be recommended for precise work.

The reverse titration is only accurate if the major portion of the ferrocyanide is added very rapidly. This method cannot therefore be recommended for general application.

The presence of a small quantity of ferric iron in the ceric solution causes a greenish coloration (ferric ferrocyanide) which disappears sharply at the end-point of the oxidation of the ferrocyanide. This visual end-point is practically identical with the potentiometric one.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

SINGLE CRYSTALS OF SILVER

BY E. W. R. STEACIE AND F. J. TOOLE

RECEIVED NOVEMBER 13, 1928 PUBLISHED APRIL 5, 1929

A large number of metallic single crystals have been prepared. Hauser[1] has obtained symmetrical etch figures on spherical single crystals of copper and silver which show the crystallographic form of the metal. Various other workers have obtained rods or wires which consisted of one crystal. As far as we are aware, however, large single metallic crystals possessing the characteristic external form have not been previously prepared.

Experimental

During the course of another investigation[2] some very pure silver was prepared. The method of preparation was to dissolve silver nitrate in water and allow the solution to settle: Silver chloride was precipitated from the filtered solution by the addition of hydrochloric acid. It was then reduced to the metal by boiling with invert sugar and sodium hydroxide. The precipitate was thoroughly washed with hot distilled water and fused to a button in a crucible under borax. Analysis of the purified silver showed 0.003% of copper, **0.001%** of lead and a trace of iron.

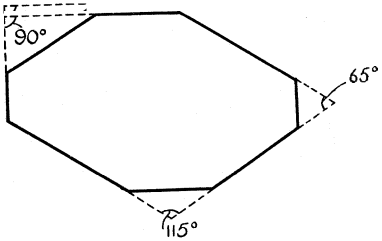


Fig. 1.—Cross section through prism.

A sample of this, weighing about **30** g., was accidentally fused owing to the failure of a thermostat, and was then cooled very slowly and kept just below the melting point for several days. The ingot, which was about 4 cm. long and **1** cm. in diameter, was treated with dilute nitric acid. After the action had continued for some time it was noticed that faces had appeared on the metal, and on examination it was found to be an octagonal prism weighing about 7 g. The crystal form is described later.

Apparently the original bar of silver consisted of a single crystal and the acid attacked the different faces in a specific manner, finally yielding an octagonal prism.

The fact that a well-defined crystal was obtained was undoubtedly due to the high degree of purity of the silver, which prevented any local electrolytic action such as would take place if impurities were present.

Hauser's crystals, prepared similarly by slow cooling, were turned into spheres on a lathe and then etched superficially with acids. The crystal-

---

[1] Hauser, *Ber. Siemens Konzern,* 1927.

[2] *Proc. Roy. Soc., London,* **117A, 662 (1928).**

line form was inferred from the shape of the resulting etch figures; in no case was the external form characteristic of the crystal obtained.

The preparation of crystals in this manner was repeated. Twenty grams of silver was placed in a quartz bulb in an electric furnace. The silver was melted and thoroughly evacuated to prevent spitting on solidification. It was necessary to shake the bulb during evacuation in order to prevent small bubbles of gas from sticking to the walls below the surface of the silver and causing irregularities in the ingot. The metal was then slowly cooled (about 5" per hour) and kept at a temperature of 940° for forty-eight hours. On treating with dilute nitric acid a crystal similar to the previous one, weighing about 4 g., was obtained.

In order to prepare satisfactory crystals it is necessary that the cooling should be slow and preferably from the bottom of the tube in order to avoid a pit at the surface. The presence of oxygen must be avoided.

We are indebted to Dr. R. P. D. Graham, Professor of Mineralogy at McGill University, who kindly examined the crystals and reported as follows.

> "The two crystals examined are prismatic in habit. Each has a diameter of about $^1/_4$ inch, and they are, respectively, $^7/_8$ inch and $^5/_8$ inch in length.
>
> "On both, there are eight faces in the prism zone, and some of them are surprisingly flat, although none are sufficiently so to yield images on the reflecting goniometer. Other faces are somewhat concave and irregularly pitted.
>
> "The longer crystal is terminated at one end by four ill-defined planes of the latter type, which form a pyramid whose apex is replaced by a tiny smooth face at right angles to the prism. The relation of these terminal faces to the eight faces of the prism zone is such as to suggest that the crystal is a combination of cube and dodecahedron elongated in the direction of a cubic axis. If such is the case, however, the crystal is highly distorted, as the angle between adjacent faces in the prism zone is not 45°, as it should be if they represent faces of the cube and dodecahedron.
>
> "Of these faces in the prism zone, four, taken alternately, are inclined to one another at 90°, and assuming the four terminal faces to be faces of the dodecahedron, these four prism faces also belong to the dodecahedron.
>
> "The remaining four faces in the prism zone are symmetrically disposed with regard to the first set, and together they would form a prism having an angle of about 65°. If, therefore, they arc faces of the cube, the crystal is much distorted. There is nothing, however, to indicate that the crystals are twinned. It is possible that the faces represent the development of two pairs of faces belonging to a four-faced cube (tetrahexahedron). The angle $hk0:kh0$ for the four-faced cube (510)is 67° 23′, and for the form (410) it is 61° $55^3/_4$′. The latter form has been observed on crystals of native silver."

Summary

Single crystals of silver can be prepared by slow cooling of the molten metal. Dilute acid attacks the faces in a specific manner, yielding prismatic crystals.

MONTREAL, CANADA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 202]

REACTIONS WITH VERY LARGE APPARENT TEMPERATURE COEFFICIENTS

BY LOUIS S. KASSEL[1]

RECEIVED NOVEMBER 27, 1928 PUBLISHED APRIL 5, 1929

During the last few months three reactions, of widely different types, have been reported to exhibit a dependence upon temperature considerably greater than is usual. R. P. Bell[2] studied the oxidation of benzoyltoluidine by potassium permanganate; the reaction taking place at a benzene–water interface; he reported a temperature coefficient of **13** for this reaction. The present author[3] has been unable to duplicate his results, and finds instead a value of about 2. Topley and Hume[4] investigated the dehydration of calcium carbonate hexahydrate crystals in the presence of liquid water; the reaction is apparently propagated throughout the separate crystals from active centers and the linear rate of propagation has a temperature coefficient of about 12. Patterson and McAlpine[5] have published measurements on the rate of decomposition of bornyl naphthalene-β-sulfonate, menthyl benzenesulfonate and menthyl naphthalene-β-sulfonate in toluene, nitrobenzene, ethylene dibromide, pyridine and methyl, ethyl, n-propyl, n-butyl and *sec.*-butyl alcohols. They did not investigate the effect of varying concentration or varying time of reaction (all their runs were for one hour), but only the dependence of percentage decomposition upon temperature. For the alcohols and pyridine they found a normal temperature coefficient, for toluene a very low one, while for ethylene dibromide and nitrobenzene the apparent temperature coefficient starts at a low value and increases rapidly; in a typical case, it increases from 1.5 to 150 in a 20° temperature range.

The purpose of the present paper is to discuss these latter measurements, to show how they may be accounted for by reactions with normal values for their separate temperature coefficients, and to make such other remarks upon the general nature of chemical reactions as the experiments suggest.

The Decomposition of Calcium Carbonate **Hexahydrate.**—Topley and Hume[4] have interpreted their experimental results to mean that the reaction is propagated throughout any given small crystal from reaction centers which arise on its surface; they have determined the approximate linear rate of propagation which this hypothesis requires and find

---

[1] National Research Fellow in Chemistry.

[2] Bell, *J. Phys. Chem.*, *32*, 882 (1928).

[3] Kassel and Schaffer, THIS JOURNAL, 51, 965 (1929).

[4] Topley and Hume, *Proc. Roy. Soc. London*, **120A,** 211 (1928).

[5] Patterson and McAlpine, *J. Chem. Soc.*, 2464 (1928).

that at 0° the reaction front advances 0.135 layer of molecules per second. If we attempt to find a mechanism which will give this rather rapid rate, and at the same time account for the high temperature coefficient, considerable difficulty is encountered. By assigning a reasonable value to the vibration frequency, Topley and Hume calculated the fraction of the vibrations, β, which resulted in decomposition; they found 2.7×10^{-14}. They then pointed out that if reaction followed upon activation at a single degree of freedom, the expected value of β would be 10^{-33}, and even if, in analogy to the theory of unimolecular gas reactions, it was supposed that every molecule which acquired sufficient energy in 11 degrees of freedom (22 energy terms) decomposed, they found a value of β of only 2×10^{-25}.

It is possible to extend these calculations somewhat, on the basis of the more satisfactory form of the unimolecular reaction theory which has been given by Rice and Ramsperger and the author.[6] First it is found that, if the classical form of the theory is to be used, the number of degrees of freedom is to be taken as not more than half of the theoretically possible number; now $CaCO_3 \cdot 6H_2O$ has 23 atoms and therefore 63 internal degrees of freedom. Hence in our calculations we will take 30 degrees of freedom instead of the 11 used by Topley and Hume. We may now distinguish two possible courses which the reaction could take. It might be that practically every activation resulted in decomposition, that is, that during the time of a single vibration an activated molecule was almost sure to decompose. In this case the rate of reaction is equal to the rate of activation, and the fraction β of all vibrations resulting in reaction is simply the fraction W_E of the molecules which contain energy in excess of the critical energy E at any instant. If we have 30 degrees of freedom, $E = 41{,}300 + 29RT$, approximately. This gives $E = 57{,}000$, and at 0° $W_E = 10^{-18}$. This is still less than β by a considerable factor, which could not be changed much by any reasonable increase in the number of degrees of freedom.

A second possibility is that only a few of the activated molecules decompose. Then if the specific reaction rate depends upon the total energy in the way that the author has given for gas reactions, the mathematical theory of these reactions may be used without change. In particular, the simple relation $d \ln K/dT = E/RT^2$ is approximately restored. We calculate that $W_E = 5 \times 10^{-10}$, which is actually large compared to β. Thus the theory is self-consistent. There is nevertheless a very serious objection to this interpretation. If we consider only the molecules in the reaction front, and write for their reaction rate $K = Ae^{-E/RT}$, we calculate that $A = 10^{32}$. This value should be comparable with that

---

[6] **Rice** and Ramsperger, THIS JOURNAL, 49, 1617 (1927); 50, 617 (1928); **Rice,** *Proc. Nat. Acad. Sci.*, *14*, 113, 118 (1928); Kassel, *J. Phys. Chem.*, 32, 225, 1065 (1928).

of the same quantity in the unimolecular gas reactions. For the eight such reactions now well established, A ranges from 3×10^{11} to 9×10^{15}.[7] It seems rather unlikely, therefore, that a value as great as would be required here is acceptable. It is possible to say roughly what the physical meaning of A is; a large value of A means that the rate of transfer of energy within a molecule from one part to another is high; in terms of the quantum mechanics, this seems to mean that the interaction energy of the various oscillators is large. One would expect, from a general chemical standpoint, that the interaction energy would be less for a rather unstable coordination compound such as calcium carbonate hexahydrate than for a stable organic molecule. Azo-*iso*propane, with 22 atoms, is directly comparable with calcium carbonate hexahydrate, with 23; and azo-isopropane has $A = 4 \times 10^{14}$. On this basis it seems to the author necessary to reject the foregoing mechanism.

Thus it does not seem satisfactory to regard this dehydration as a single reaction with an energy of activation of approximately 40,000 calories. An alternative view is that the reaction occurs in steps. Now Topley and Hume have stated that there is no evidence for the existence of intermediate hydrates, but this only means that they do not occur in very large amount. We are dealing here with a surface reaction, and it would seem quite possible for an appreciable amount of the reaction front to consist of lower hydrates without any direct evidence of their existence being obtained. It remains to be seen whether a stepwise dehydration offers a satisfactory explanation of the temperature coefficient.

It is perhaps rather unlikely that the actual dehydration should require as many as six steps; partly for this reason, but more for the sake of simplicity, we shall consider the simpler case of a compound AB_3. We assume that the following reactions occur: (1) $AB3 = AB_2 + B$; (2) $AB_2 = AB + B$; (3) $AB = A + B$; (4) $AB_2 + B = AB_3$; (5) $AB + B = AB_2$. B corresponds to the water, which is always present during the experiments, and we may take its concentration to be constant and absorb it into the reaction rate constants. 'She other substances are all solids. We shall suppose that the reaction starts at an active center, perhaps a fault in the crystal, and is propagated from it in the following way: the layer of molecules surrounding this center is at liberty to react according to the scheme given above. When the reaction in this layer has acquired a definite degree of completion, the next layer starts to react; and this process continues until the entire crystal has decomposed. We further suppose that the first three reactions above all have the rate constant p, and that the last two have the constant q, where $p \ll q$. It is possible to carry through the analysis using different constants for each reaction, but there does not seem to be any profit in such a complication.

[7] Kassel, THIS JOURNAL, **50,** 1351 (1928).

Now for a layer just beginning to react we may write down the following equations

$$\frac{dx}{dt} = -px + qy \tag{1}$$

$$\frac{dy}{dt} = px - (q+p)y + qz \tag{2}$$

$$\frac{dz}{dt} = py - (q+p)z \tag{3}$$

$$\frac{dD}{dt} = pz \tag{4}$$

$$x(0) = a, \quad y(0) = z(0) = D(0) = 0 \tag{5}$$

where

$$x = [\mathrm{AB_3}], \quad y = [\mathrm{AB_2}], \quad z = [\mathrm{AB}], \quad D = [\mathrm{A}]$$

The symbol [ ] here means a *surface* concentration. To solve these equations for D it is most convenient to solve the first three of them for x. We differentiate (2) once, and (3) twice, and eliminate x and y and their derivatives from the six equations (1), (2), (2′), (3), (3′) and (3″). The resulting equation is

$$\frac{d^3z}{dt^3} + (2q+3p)\frac{d^2z}{dt^2} + (q^2+2pq+3p^2)\frac{dz}{dt} + p^3 = 0$$

It is well known that the general solution of (6) is

$$Z = Ae^{-m_1t} + Be^{-m_2t} + Ce^{-m_3t}$$

where m_1, m_2, and m_3 are the roots of

$$m^3 + (2q+3p)m^2 + (q^2+2pq+3p^2)m + p^3 = 0$$

The exact expressions for these roots are too unwieldy to use; it is more convenient to make use of the fact that $p \ll q$ and write down the approximate values.

$$m_1 = -p\left[\frac{p^2}{q^2+2pq+3p^2} + \text{terms in } \left(\frac{p}{q}\right)^5\right]$$

$$m_2 = -q\left[1 + \frac{3}{2}\frac{p}{q} - \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} + \text{terms in } \left(\frac{p}{q}\right)^{5/2}\right]$$

$$m_3 = -q\left[1 + \frac{3}{2}\frac{p}{q} + \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} + \text{terms in } \left(\frac{p}{q}\right)^{5/2}\right]$$

If we adopt the notation

$$\frac{p^2}{q^2+2pq+3p^2} = F \qquad 1 + \frac{3}{2}\frac{p}{q} = S \qquad \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} = R$$

these become, to the same approximation as before

$$m_1 = pF + \dots \qquad \begin{aligned} m_2 &= -q[S - R + \dots] \\ m_3 &= -q[S + R + \dots] \end{aligned}$$

It remains to evaluate the constants A, B and C. We know that at $t = 0$, $z = 0$, and it may also be shown that the initial conditions require $dz/dt = 0$. These conditions will be satisfied if

$$A + B + C = 0 \qquad -pFA - q(S-R)B - q(S+R)C = 0$$

Hence

$$C = \frac{S-R}{2R}A; \quad B = \frac{S+R}{2R}A$$

It is now easy to get D by integration; we find

$$\frac{D}{A} = \frac{1}{F}\{1 - e^{-pFt}\} - \frac{S+R}{S-R} \times \frac{p}{2qR}\{1 - e^{-q(S-R)t}\} + \frac{S-R}{S+R} \times \frac{p}{2qR}\{1 - e^{-q(S+R)t}\}$$

For small values of t all the terms must be considered, but when t is larger the first one becomes dominant; in fact, during almost the entire course of the reaction the other two terms are entirely negligible. The course of the reaction is shown in the following table for the special case $p = 0.01q$.

TABLE I

COURSE OF THE REACTION

qt	T_1	T_2	T_3	D/A
0.1	0.001	−0,00535	0.00438	0.00003
1.0	.01	− .03664	.02770	.00106
10.9	.10	− .06111	.04122	.08011
1000.0	10.00	− .Of3111	.04122	9.980
100000.0	952.9	− .06111	.04122	952.9
∞	10203	− .06111	.04122	10203

Here $T_1 = \frac{1}{F}\{1 - e^{-pFt}\}$

$$T_2 = -\frac{S+R}{S-R} \times \frac{p}{2qR}\{1 - e^{-q(S-R)t}\} \qquad T_3 = \frac{S-R}{S+R} \times \frac{p}{2qR}\{1 - e^{-q(S+R)t}\}$$

It is evident from this table that for all practical purposes, except when we are interested in the initial stage of the reaction, we need consider only the first term; but this term corresponds to a reaction with a rate constant given by

$$k = pF = p^3/(q^2 + 2pq + 3p^2)$$

We wish now to see whether this mechanism is in agreement with the experimental facts for the case of calcium carbonate hexahydrate. First we notice that it is possible to account for the temperature coefficient. If we put $p_1 = 0.01\,q_1$; $p_2 = 3p_1$; $q_2 = 1.5q_1$, where the subscripts 1 and 2 refer to temperatures 10° apart, we find $k_2 = 11.76\,k_1$. That is, if the dissociations have a temperature coefficient of 3, and the associations a temperature coefficient of 1.5, that of the overall reaction will be 11.76.

We must next show that it is possible for the dissociations to take place fast enough. The reaction front passes over 0.135 layer of molecules per second at 0°. If we suppose that the reaction begins in the next layer when the hydrate has been reduced to $1/e$ of its original concentration, and also that $p = 0.01\,q$, we can easily calculate that $p = 1350$. Then, writing $p = Ae^{-E/RT}$, and choosing E to make the temperature coefficient 3, we get E = 16,200 calories and $A = 10^{15}$. This value for A is reasonable and our experience in calculating the rates of unimolecular gas reactions convinces us that there will be no difficulty in producing activation fast enough.

It is also worth noticing that the reverse reactions can occur as fast as we have postulated. A temperature coefficient of 1.5 corresponds to an energy of activation of 6000 calories, and if we calculate the bimolecular rate in the manner used so successfully by Hinshelwood for gas reactions we find that 10^{-5} of the collisions could lead to combination. The actual bimolecular rate that we have assumed is 135,000; it seems reasonable to take the number of collisions per second equal to the vibration frequency, which Topley and Hume estimated as 5×10^{12}; if we do this we find that the fraction of successful collisions need only be 3×10^{-8}. It is, of course, not a source of difficulty that there are fewer successful collisions than would seem possible; if there had been an inequality in the other direction the scheme would have required modification.

It thus appears that the foregoing tentative explanation of the decomposition of calcium carbonate hexahydrate is perfectly consistent. There is no direct evidence supporting it, and it would seem very difficult to obtain any. Its chief merit is that it is one way, and the only way known at present, to account for the experimental results in this reaction; it shows that these results do not require any additions to the general reaction rate theory, as might at first sight be supposed.

The Decomposition of Menthyl and Bornyl Esters.—The work of Patterson and McAlpine was more from the organic than from the kinetic standpoint. They did not determine the order of the reactions and therefore did not calculate any reaction rate constants. In our analysis of their data we will first suppose that there is a homogeneous unimolecular decomposition, and calculate constants on that basis. For each ester–solvent combination we obtain a series of constants, one at each temperature. The results are of three types, illustrated by the following tables.

TABLE II

DECOMPOSITION OF MENTHYL BENZENESULFONATE IN TOLUENE

Temperature, °C.	85		90		95		100		105
% Decomp. = x	0.98		1.04		1.06		2.23		2.37
Log 100/(100 − x)	0.00428		0.00454		0.00463		0.00979		0.01042
E_0		3100		1100		40900		3500	

TABLE III

DECOMPOSITION OF MENTHYL BENZENESULRONATE IN NITROBENZENE

Temperature °C.	85		90		95		100		105
% Decomp. = x	2.37		2.75		5.88		12.87		82.15
Log 100/(100 − x)	0.01042		0.01211		0.02632		0.05983		0.74836
E_0		7870		40800		45600		140000	

TABLE IV

DECOMPOSITION OF MENTHYL BENZENESULFONATE IN BUTYL ALCOHOL

Temperature °C.	75	80	85	90	95	100	105
% Decomp. = x	4.10	6.77	10.85	17.27	28.15	45.14	60.23
Log $100/(100-x)$	0.01818	0.03044	0.04988	0.08234	0.14367	0.26074	0.40044
E_0		25200	24800	26000	29600	32600	24000

In these tables the first two lines are taken directly from the paper of Patterson and McAlpine; the numbers in the third line are proportional to the calculated unimolecular constants and those in the last are the values of the energy of activation calculated from the constants at two successive temperatures by the Arrhenius equation. Before proceeding further it may be well to point out that if constants were calculated for a bimolecular reaction, they would increase more rapidly at the higher temperatures where the reaction goes nearly to completion. Thus, if the data in Table III are calculated on the basis of a bimolecular reaction, the heat of activation for the first interval is unchanged, while that for the last is increased from 140,000 to 200,000, this latter value corresponding to a 31-fold increase in the rate for 5°. There are other cases in which the change is still more marked.

There does not seem to be any trend in the values of the heat of activation in Table IV. Similar results are found for each of the three esters whenever the solvent is an alcohol or pyridine. The average value of the energy of activation for each of the ester–solvent combinations of this type comes out 25,000 to 27,000 calories, which is to be considered as constant within the experimental error. It therefore seems altogether likely that the reaction is truly unimolecular in these solvents.

With nitrobenzene and ethylene dibromide as solvents, the results follow the type of Table III, in several cases with still more startling increases in the energy of activation. When an apparent increase in the energy of activation with increase in temperature is observed, it is usually to be ascribed to two reactions, either simultaneous or successive. Then in the normal case the energies of activation observed will be intermediate between the true energies of activation of the separate reactions; but since an energy of activation of 140,000 calories, corresponding as it does to a temperature coefficient of about 150, is utterly out of the question, it becomes necessary to seek some other explanation of the results. It occurred to the author that the reaction in these solvents might be autocatalytic. Investigation proved that it was actually possible to account for the type of result observed by a mechanism of this sort. If we write $dx/dt = a(A - x) + b(A - x)x$ and solve for x at $t = 1$, we find $x/A = (P - 1)/(P + R)$, where $R = bA/a$ and $P = e^{a(R+1)}$. Now if we assume appropriate values of a and R and let them vary with the temperature in the normal way, we can get x/A to have the type of temperature coefficient found experimentally. Two ways in which this may be done are shown in Table V.

TABLE V

CALCULATED RESULTS

(a)				(b)			
a	*R*	*Ab*	*x/A*	*a*	R	*Ab*	*x/A*
0.027	2.5	0.067	0.0275	0.027	10.24	0.276	0.0306
.036	5.0	.180	.0386	.036	17.92	.645	.0491
.048	10.0	.480	.0589	.048	31.36	1.51	.1033
.064	20.0	1.28	.1189	.064	54.88	3.51	.3834
.0853	40.0	3.41	.4385	.0853	96.04	8.19	.9739
.1137	80.0	9.10	.9920				

If it is supposed that the intervals in this table represent 5°, then the 10" temperature coefficient for the uncatalyzed reactions is $(4/3)^2$ or 1.78 in both cases; in (a) that for the catalyzed reaction is $(2\ X\ 4/3)^2$ or 7.11, while in (b) it is $(7/4\ X\ 4/3)^2$ or 5.44. It is not impossible that the catalyst should enter into the equation as a square, in which case somewhat smaller temperature coefficients for the catalyzed reaction would suffice; but there is no great objection to a value of 5 or so, and here again it must he urged that no importance attaches to the details of the calculation, only the general result being significant. It thus appears possible to account for the experimental results in nitrobenzene and ethylene dibromide by a combination of an uncatalyzed, probably unimolecular decomposition with a temperature coefficient in the neighborhood of 2, with a simultaneous decomposition, catalyzed by one of the reaction products, with a temperature coefficient that may be as great as 5 or 6, but may be somewhat lower.

It is hard to draw any definite conclusion about the decomposition in toluene; the sudden increase in rate between 95 and 100° shown in Table II is surely due to accumulated experimental error, and the table as a whole suggests a temperature coefficient of about 1.5; the other two esters have been studied over ranges of but 5 and 10°, respectively, and both show a temperature coefficient from 1.00 to 1.05. It is not at all certain whether the difference is real or not. A temperature coefficient of 1.2 or less would suggest heterogeneous catalysis, either by the walls or by dust particles, but there can be no certainty as to this without further data.

We have thus been able to account moderately well for all the experimental results by assuming three different types of decomposition: a heterogeneous catalyzed reaction, a homogeneous uncatalyzed one and a homogeneous catalysis by the reaction products. An explanation of this character cannot be considered satisfactory unless reasons can be produced for the changing importance of the various types as the solvent is changed. This is not hard to do; Patterson and McAlpine state that the products of the decomposition are a sulfonic acid and such substances as camphene and dibornylene as well as more complex hydrocarbon residues. Now hydrogen ion, and in particular unsolvated hydrogen ion, is the most notorious catalyst in all organic chemistry and it may well be the catalyst here. It is well known that pyridine and alcohol form complex ions with H^+ and the catalysis would thus be reduced in these solvents; the extent of the reduction is not easily predictable, but it is not surprising that the catalytic action is in fact practically stopped. Nitrobenzene and ethylene dibromide do not combine with H^+ to any appreciable extent, and thus in these solvents the catalysis is marked. We should expect it to be important in toluene also, but since in this solvent the decomposition obtained was always slight, it is impossible to tell whether this prediction is verified. The magnitude of the uncatalyzed reaction also varies in about the way we expect; it is greatest in the alcohols, which are the most polar solvents used, and greatest of all in methyl alcohol. In nitrobenzene, pyridine and ethylene dibromide the uncatalyzed rate is about the same, considerably less than in even butyl alcohol, while in toluene it is very much less than in any of the other solvents. The electric moment of the nitrobenzene molecule is known to be some 7 or 8 times that of toluene, so that the rate should be greater in nitrobenzene. Ethylene dibromide is symmetrical and should have a small or zero moment; there does not seem to be any available data as to this. If there is a wall reaction or a dust reaction it is probably independent of the solvent, but even though the entire reaction in toluene is due to this source, it would not be of importance in any of the other solvents. The qualitative variation of reaction rate with solvent for these decompositions is thus seen to be in agreement with theoretical predictions.

The remaining uncertainties as to the mechanism of these reactions could almost certainly be cleared up by a study from the kinetic standpoint. It does not appear to the author, however, of great importance that this should be done. The preceding analysis seems to leave little doubt that all the facts can be accounted for without introducing any new principles into reaction rate theory.

Summary

1. The possibility of regarding the decomposition of calcium carbonate hexahydrate crystals as a single reaction with a temperature coefficient of about 12 has been discussed; it appears that a reaction of this character is very improbable. It is then shown how the experimental results can be accounted for by assuming that the reaction occurs in steps, all but the last one being reversible.

2. The apparently strange behavior of the temperature coefficient of reaction rate in the decomposition of bornyl and menthyl sulfonates in certain solvents has been accounted for on the basis of autocatalysis by the resulting acid, and the general effect of the solvent upon these reactions bas been shown to agree with predictions based on the character of the solvent.

PASADENA, CALIPORNIA

[CONTRIBUTION PROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES OF ISOPROPYL ALCOHOL AND ACETONE FROM 16 TO 298°K. AND THE CORRESPONDING ENTROPIES AND FREE ENERGIES

BY KENNETH K. KELLEY[1]

RECEIVED NOVEMBER 28, 1928 PUBLISHED APRIL 5, 1929

The heat capacities of isopropyl alcohol and acetone have been studied by Parks and the author[2] from 70 to 298°K. Equilibrium measurements at several temperatures were also made for the reaction $CH_3CHOHCH_3 = CH_3COCH_3 + H_2$ in the gaseous state[3] in order to show that the third law of thermodynamics held, at least for all practical purposes, for this organic reaction. An exact test was not possible since heat capacity data for gaseous isopropyl alcohol and acetone were not available for extrapolating the results of the equilibrium measurements and since considerable uncertainty was involved in extending the heat capacity curves for crystalline isopropyl alcohol and acetone below 70°K. The present work, carrying the specific heat measurements to 16°K., was undertaken to remedy this latter defect. The temperature range covered before has been reinvestigated with increased accuracy and measurements have been obtained in the large temperature gaps which were omitted in the previous work. Details of the apparatus and methods used were given in a previous paper.[4]

Materials

Isopropyl Alcohol.—The best grade of isopropyl alcohol (99 to 100%) of the Special Chemicals Company was used. It was refluxed over lime for eighteen hours and carefully fractionated three times. The middle portion taken for the measurements had a volume of about 200 cc. and a boiling-point range of 0.03". The density was $d_4^{25} = 0.78095$, while Brunel[5] found $d_4^{25} = 0.78084$ for 100% *iso*propyl alcohol. The density determination corresponds to 99.95% of alcohol on the basis of purity adopted by Parks and Kelley.

---

[1] National Research Fellow in Chemistry.

[2] Parks and Kelley, THIS JOURNAL, 47, 2089 (1925).

[3] Parks and Kelley, J. Phys. Chem., **32,** 734 (1928).

[4] Kelley, THIS JOURNAL, 51, 180 (1929).

[5] Brunel, *ibid.,* 45, 1336 (1923).

Acetone.—The acetone was an Eastman Kodak Company product. It was allowed to stand over calcium chloride for seven days, decanted off and carefully fractionated three times. The middle fraction used had a boiling point range of 0.05" and a volume of 150 cc. The density was $d_4^{25} = 0.78650$ which compares favorably with the values given in the literature.

The Specific Heats

In Tables I and II are given the results of the specific heat measurements expressed in 15° calories per mole (in vacuum). The same data are shown graphically in Figs. 1 and 2.

TABLE I

SPECIFIC HEATS OF *ISO*PROPYL ALCOHOL

1 mole = 60.06 g.

T, °K.	C_p g.-cal.$_{15}$°/mole	T, °K.	C_p g.-cal $_{15}$°/mole	T, °K.	C_p g.-cal $_{15}$°/mole
Crystals				Liquid	
19.49	1.936	82.27	11.28	188.45	25 82
23.82	2.749	90.44	11.99	193.02	26.05
26.88	3.413	99.62	12.71	202.32	26.47
29.99	4.041	107.33	13.66	212.82	26.85
34.03	4.791	115.05	14.49	224.07	27.56
38.68	5.612	123.91	15.25	235.26	28.31
43.02	6.341	131.95	15.98	246.54	29.57
46.90	6.928	136.26	16.19	258.40	30.67
51.04	7.524	144.56	17.16	274.48	32.07
55.41	8.090	153.08	18.06	280.26	33.68
68.51	9.788	161.11	19.01	286.76	34.49
72.44	10.21	165.98	19.42	292.84	35.79
77.64	10.84	170.46	20.24		

TABLE II

SPECIFIC HEATS OF ACETONE

1 mole = 58.05 *g.*

T, °K.	C_p g.-cal.$_{15}$°/mole	T, °K.	C_p g.-cal.$_{15}$°/mole	T, °K.	C_p g.-cal $_{15}$°/mole
Crystals				Liquid	
17.77	1.899	93.44	14.98	180.31	28.04
20.99	2.661	100.74	15.76	180.40	27.97
23.98	3.290	107.65	16.63	180.78	28.06
27.05	4.112	114.81	17.55	185.02	27.96
30.68	4.952	119.09	18.10	189.23	27.74
34.24	5.863	121.56a	18.93	199.19	27.77
37.55	6.613	125.58	19.79	209.31	28.17
41.07	7.429	125.61a	19.92	218.41	28.27
47.38	8.607	129.45	19.73	228.14	28.19
54.90	9.977	129.85a	19.78	242.75	28.34
61.34	11.12	133.30	19.19	258.47	28.69
67.03	11.91	143.62	19.55	272.88	29.31
70.47	12.34	151.08	19.77	282.59	29.37
74.31	12.90	158.89	19.99	296.99	29.80
78.41	13.40	163.34	20.10		
82.18	13.81	126.59x	18.55		
86.15	14.16	130.64x	18.74		

The isopropyl alcohol curves have no abnormalities and require no discussion. In the case of the acetone a curious hump occurs with the maximum at about 126°K. There can be little doubt but that some sort of a transition in the crystals involving a small energy change occurs here, for after passing through this region the material was kept at about 150°K. overnight, then rapidly cooled to 123° and the two determinations marked "x" in Table II and in Fig. 2 were obtained. During these two determinations the substance must have been in the high temperature form but supercooled somewhat. Immediately afterward the substance was further cooled to 118°K. and allowed to stand for several hours, after which the three determinations marked "a" in Table II were made. These three measurements agree very well with the previous ones around the hump and are about one calorie per mole higher than those marked "x," showing that on further cooling the substance passes into the low temperature form. A similar case has been discovered by Millar[6] in the heat capacity curve for manganese dioxide.

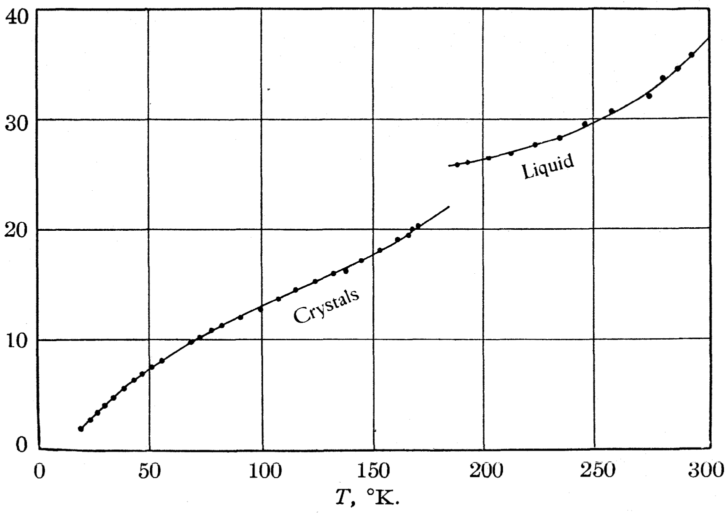


Fig. 1.—Heat capacity of isopropyl alcohol in calories per mole.

This phenomenon was missed in the work of Parks and Kelley since no measurements were made between 110 and 150°. A warming curve was taken through this region but was not accurate enough to indicate an increase in heat capacity of only 5%, though undoubtedly a transition involving a large energy change could not have escaped notice.

The facts or even a theory to explain the various types of transitions which have been found in specific heat curves would be very interesting but needless to say both are lacking at present.

[6] Millar, THIS JOURNAL, 50, 1875 (1928).

The specific heat of liquid acetone first decreases slightly just above the melting point and then increases, similarly to the behavior of water. This is usually attributed to association effects.

In an earlier paper[4] involving similar data for methyl alcohol a somewhat detailed discussion of the accuracy of the measurements was given which will also apply to the present results.

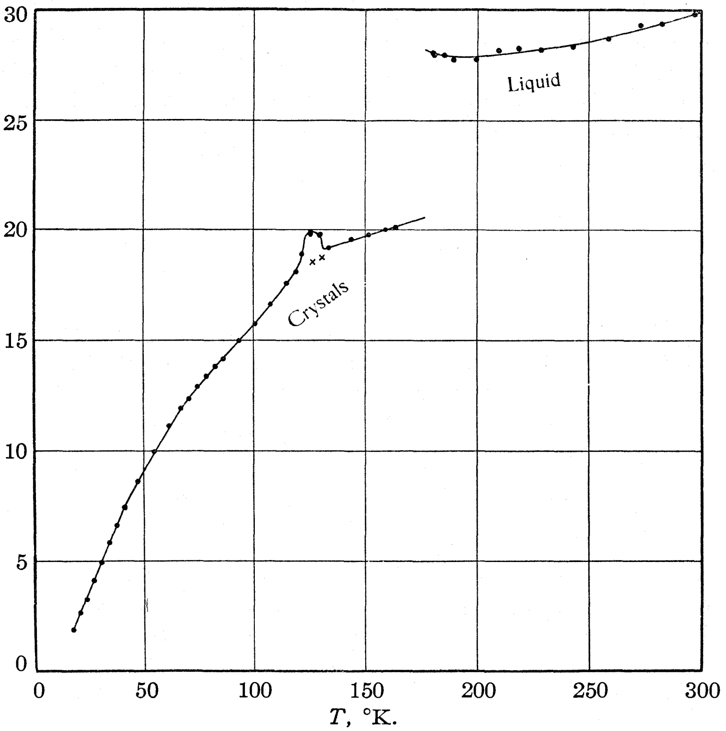


Fig. 2.—Heat capacity of acetone in calories per mole.

The Fusion Data.—The heats of fusion and the temperature of fusion were measured and the results appear in Table III.

TABLE III

HEATS OF FUSION OF *Iso*PROPYL ALCOHOL AND ACETONE

Substance	T, °K.	Heat of fusion in g.-cal.$_{15°}$ per mole 1st result	2nd result	mean
Isopropyl alcohol	184.67	1283	1285	1284
Acetone	176.62	1364	1368	1366

The mean values for the heats of fusion are considered accurate to 0.5% or better.

The Entropies.—The values of the entropies at 295.1°K. were calculated. The heat capacity curves for the crystalline substances were extrapolated from the initial temperatures of the lowest measurements to 0°K. by means of Debye functions with $\Theta = 108$ for *iso*propyl alcohol and $\Theta = 101$ for acetone. The results appear in Table IV.

TABLE IV

ENTROPIES

*Iso*propyl alcohol

0–16°K. (estrap.)	crystals	=	0.47
16–184 67	crystals	=	21.61
1284/184.67	fusion	=	6.95
184.67–298.1	liquid	=	13.99

$S_{298\cdot 1}$ for 1 mole of liquid =
43.0(±0 3) E. U.

Acetone

0–16°K. (extrap.)	crystals	=	0 56
16–176.62	crystals	=	24.67
1366/176.62	fusion	=	7.73
176.62–298 1	liquid	=	14.90

$S_{298\cdot 1}$ for 1 mole of liquid =
47.9(±0.3) E. U.

The entropy under the hump in the acetone crystals curve in excess of that due to the "normal" specific heat is 0.1 E. U. per mole.

The Free Energies.—The free energies of formation from the elements of the two substances may be calculated from the third law of thermodynamics and the thermodynamic equation, AF = AH − TAS.

There is no recent determination of the heat of combustion of *iso*propyl alcohol. Richards and Davis[7] have determined accurately the heat of combustion of the normal propyl alcohol and from this has been subtracted 5700 cal. per mole, which is the difference between the heats of combustion of the iso- and n-propyl alcohols found by Zubow.[8] Richards and Davis' value was corrected to 15° calories. The result of this procedure is 477,300 cal. per mole for isopropyl alcohol at 291°K. For the sake of consistency this value was corrected to 298°K., though the accuracy does not warrant it. Emery and Bennedict's[9] value for the heat of combustion of acetone has been utilized, correction being made to vacuum weighing and to 298°K. The final values appear in Col. 2 of Table V.

TABLE V

THERMAL DATA

The 15° g. calorie is used throughout

Substance	Heat of combustion at 298 1°K.	$\Delta H_{298\cdot 1}$	$\Delta S_{298\cdot 1}$, E. U	$\Delta F_{298\cdot 1}$
Isopropyl alcohol	477,100	−79,000	−103.7	−48,100
Acetone	430,500	−57,300	− 69.2	−36,700

Column 3 contains the values of $\Delta H_{298\cdot 1}$ which were calculated using the best available values for the heats of formation of carbon dioxide and water.[4] Column 4 contains the value of $\Delta S_{298\cdot 1}$ calculated from the experimental entropies of this paper and the entropies of the elements pre-

---

[7] Richards and Davis, THIS JOURNAL, 42, 1599 (1920).

[8] Zubow's values have been recalculated by Swietoslawski, *ibid.*, 42, 1092 (1920).

[9] Landolt, Bornstein, Roth, Scheel, "Tabellen," **1923.**

viously adopted.[4] In Col. 5 are the free energies of formation from the elements.

Discussion

The differences between the entropy values given here and those reported by Parks and Kelley[2,3] are largely due to the error in extrapolating the heat capacity curves by means of the "n" formula as was done in earlier work. The use of this formula below 90°K. causes an error of 2.1 E. U. or 17% in the extrapolation for isopropyl alcohol and 4.2 E. U. or 25% in the extrapolation for acetone. Similar results were reported for methyl alcohol[4] and for ethyl alcohol.[10]

We are now in a position to recalculate the entropy of the reaction, $CH_3CHOHCH_3(l) = CH_3COCH_3(l) + H_2(g)$, at 298.1°K. with considerably greater accuracy than was obtained by Parks and Kelley from their heat capacity measurements. We find $\Delta S_{298.1} = 47.9 + 29.6 - 43.0 = 34.5$ E. U.[11] while Parks and Kelley from the equilibrium measurements obtained 35.9 E. U. These values agree as well as could be expected in view of the fact that no heat capacity data for gaseous *iso*-propyl alcohol are available, so that a very accurate extrapolation of the results of the equilibrium measurements to 298°K. is not possible. Using the value of $\Delta H_{298.1} = 17,430$ cal. obtained by Parks and Kelley, the free energies of this reaction corresponding to the above entropy values are, respectively, 7150 cal. and 6720 cal.

Summary

1. The specific heats of isopropyl alcohol and acetone from 16 to 298°K. have been measured.
2. The heats and temperatures of fusion were determined.
3. The entropies and the free energies of formation from the elements have been calculated for 298°K.
4. The entropy and free energy of the reaction $CH_3CHOHCH_3(l) = CH_3COCH_3(l) + H_2(g)$ at 298°K. have been recalculated using the present thermal data and the third law of thermodynamics. These results are compared with previously reported data obtained by studying equilibria.

BERKELEY, CALIFORNIA

---

[10] Kelley, THIS JOURNAL, 51, 779 (1929).

[11] In a recent paper Giauque and Johnston [*ibid.*, 50, 3221 (1928)] consider that the entropy of hydrogen should be increased by 4.39 E. U. at 298.1°K. However, it is possible that only 1.63 E. U. of this need be considered for chemical reactions (Giauque, personal communication). Such a change would increase the third law value of the entropy of this reaction to 36.1 E. U., which agrees better with the equilibrium measurements.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXVII. GERMANIUM DICHLORIDE[1]

BY L. M. DENNIS AND H. L. HUNTER

RECEIVED DECEMBER 1, 1928 PUBLISHED APRIL 5, 1929

Introduction

Winkler stated[2] in 1886 that germanium dichloride is formed when hydrogen chloride is passed over heated germanium. In the following year he announced[3] that the product of this reaction is germanium chloroform and not germanium dichloride. It has since been ascertained by Laubengayer[4] that in the reaction employed by Winkler both germanium chloroform, $GeHCl_3$, and germanium tetrachloride are formed, and that these two substances are not separable by long-continued fractionation in the vacuum apparatus.[5] Germanium chloroform was finally prepared by Tabern[4] by passing the vapor of germanium tetrachloride over heated germanium, which formed what was presumably germanium dichloride, and then causing this product to unite with hydrogen chloride. Tabern made a preliminary study of the germanium dichloride and the extension of our knowledge of this interesting substance was the objective of the present investigation.

Experimental

Germanium chloroform is readily hydrolyzed by water with the formation of hydrated germanous oxide (GeO) and hydrochloric acid, whereas silicon chloroform yields upon hydrolysis silicon dioxide and hydrogen. It was therefore thought possible to prepare germanium dichloride from the chloroform by removing from the latter an atom of chlorine and the atom of hydrogen. This was tried with a number of different substances but germanium dichloride was not obtained.

Attempts were next made to reduce germanium tetrachloride by various powerful reducing agents, but in no case was there definite evidence of the formation of the dichloride. Because of the negative character of these results, the method that was employed in the preparation of $GeHCl_3$ (see above) was then again taken up: $Ge + GeCl_4 = 2GeCl_2$.

Metallic germanium[6] was powdered and fused under salt to remove so far as possible traces of germanium dioxide that it might contain. The resulting button of metal was finely powdered.

---

[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by H. L. Hunter in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Winkler, *J. prakt. Chem.*, 142 (N. S. 34) 222 (1886).

[3] Winkler, *ibid.*, 144 (N. S. 36) 188 (1887).

[4] Dennis, Orndorff and Tabern, *J. Phys. Chem.*, 30, 1049 (1926).

[5] Laubengayer and Corey, *ibid.*, 30, 1043 (1926).

[6] Prepared by the method of Tressler and Dennis, *ibid.*, 31, 1429 (1927).

Germanium tetrachloride[7] was freed from hydrochloric acid by first passing air through it at 40° and then distilling it over into a bulb containing solid sodium carbonate and calcium chloride. Some hours of contact with these substances removes water and the last traces of hydrogen chloride. The purified germanium tetrachloride was then distilled into the bulb M, while that bulb was still attached to the vacuum apparatus[5] by a "normal" interchangeable slip-joint.

The apparatus that was used for carrying out the reaction is shown in Fig. 1. The tube AB is of pyrex glass. All other parts are of soft glass. The ground slip-joints are "normal," interchangeable connections. The pyrex tube is joined to the soft-glass tubes by pieces of "varnished" rubber tubing which can withstand high pressures and is quite impervious to gases.

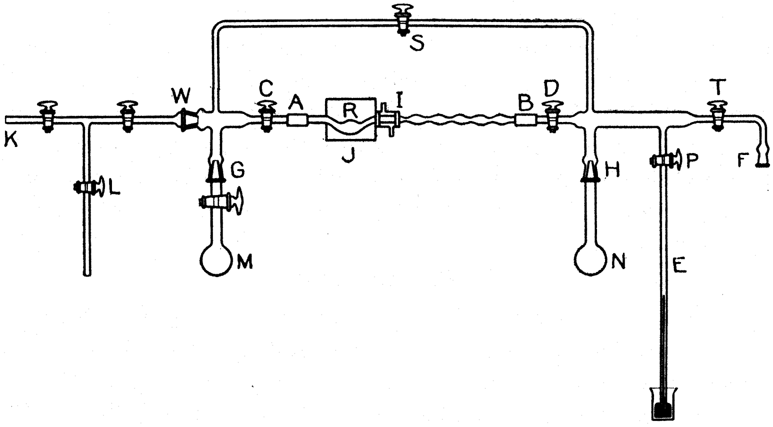


Fig. 1.

The metallic germanium was placed in a widened part of the tube, R, which is surrounded by an electric furnace, J. A short water-jacket, through which water can be run, surrounds the tube just beyond the furnace.

The germanium tetrachloride was solidified by cooling the bulb M with liquid air while it was still attached to the fractionating apparatus, the stopcock was closed and the bulb was then slipped off from that apparatus and attached to the chain (Fig. 1) by the "normal" joint at G. While the tetrachloride was kept frozen, the whole apparatus was exhausted by a pump through K. The stopcock S was then closed.

The current was now turned on the furnace, the temperature being measured by a thermometer or thermocouple throughout the experiment. When the furnace temperature had reached 300°, the stopcocks C and D were opened and the germanium tetrachloride was slowly distilled through the tube into the bulb N by surrounding the latter with a refrigerant and removing the liquid air from around M.

Reaction began at 350°, a white deposit appearing at I just beyond the water-jacket. The temperature of the furnace was held at about 430°. After all of the liquid had distilled over into N, the stopcocks C and D were closed, S was opened and the tetrachloride was returned to M by cooling this bulb and warming N. This

---

[7] Prepared by the method of Tabern, Orndorff and Dennis, THIS JOURNAL, 47, 2040 (1925).

procedure was repeated until a sufficient amount of the white deposit had collected in the tube between I and B. The excess of germanium tetrachloride was then removed from the tube by cooling the bulb M with liquid air and closing the stopcock of the bulb after condensation was complete.

Analysis.—Since germanium dichloride is instantly decomposed by moisture and is slowly acted upon by oxygen, the sampies for analysis were obtained by passing dry nitrogen through the tube, AB, and breaking off sections of the tube at the constrictions, dropping each segment immediately into a dry weighing bottle that stood in a desiccator filled with nitrogen. The bottle was stoppered and weighed, and the segment of tube was then dropped into a solution of sodium hydroxide to which had been added an amount of hydrogen peroxide sufficient to oxidize the sample. After solution was complete, chlorine was precipitated by silver nitrate, the excess of silver was removed from the filtrate by hydrochloric acid, sulfuric acid was added to the resulting solution until the acid concentration was 6 *N* and germanium was precipitated as the white disulfide.

Anal. Subs., 0.0695, 0.3101. Calcd. for $GeCl_2$: Cl, 0.03434, 0.1532; Ge, 0.0351, 0.1569. Found: Cl, 0.0343, 0.1530; Ge, 0.0350, 0.1558.

Properties.—At room temperature germanium dichloride in a thin layer is almost white; the color deepens through a cream to a light yellow tint as the layer becomes thicker. When some of the compound was caused to deposit on the sides of a thin-walled test-tube, and the tube was evacuated and then heated in an oil-bath, dissociation of the dichloride began at 74.6°, and as the temperature rose the substance became first cream-colored, then lemon-yellow, orange, reddish-brown, dark brown, and finally black at about 450°, at which temperature dissociation into $GeCl_4$ and Ge was complete. Because of this ease of dissociation, the compound cannot be sublimed either in a vacuum or in a current of an inert gas.

Germanium dichloride is insoluble in, or reacts with, many of the usual solvents that were added to it. It is not affected by 95% ethyl alcohol or by chloroform. It is fairly soluble in germanium tetrachloride. Water hydrolyzes it, and ammonium hydroxide converts it to an orange-colored substance. Concentrated hydrochloric acid changes it to a white solid which soon dissolves in the acid, with the probable formation of trichloromonogermane.

Dry oxygen slowly acts upon germanium dichloride. After about fifteen minutes' contact, the dichloride begins to turn white, due to the formation of germanium dioxide. A volatile substance that is simultaneously formed was identified as germanium tetrachloride (mol. wt., 213. Theoretical, 214.4). This reaction is, therefore, $2GeCl_2 + O_2 = GeO_2 + GeCl_4$.

When moist oxygen is passed over the compound, the reaction shown in the preceding equation probably takes place to a slight extent, but the moisture acts much more vigorously on the substance than does the oxygen. The first stage is doubtless $GeCl_2 + 2H_2O = Ge(OH)_2 + 2HCl$. The hydrogen chloride then instantly combines with unchanged germanium dichloride to form germanium chloroform, which is carried out of the tube by the current of oxygen.

Chlorine rapidly attacks germanium dichloride with the formation of pure germanium tetrachloride. Bromine forms a colorless liquid, which on fractionation was found to consist almost entirely of germanium tetrachloride and tetrabromide. Not more than a trace of a double halide was produced. Hydrogen sulfide acts at once upon germanium dichloride at room temperature. Quantitative examination of the products showed that the reaction is essentially $GeCl_2 + H_2S = GeS + 2HCl$.

Summary

This article describes the preparation and properties of germanium dichloride.

ITHACA, NEW YORK

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

A CONDUCTANCE-DIFFUSION METHOD FOR STUDYING THE COAGULATION OF COLLOIDAL FERRIC OXIDE[1,2]

BY C. HARVEY SORUM

RECEIVED DECEMBER 3, 1928 PUBLISHED APRIL 5, 1929

Introduction

The knowledge that electrolytes will coagulate colloids dates back to the work of Thomas Graham.[3] The study of this particular phenomenon from all of its various angles has proceeded almost without a halt from Graham's time up to the present, with the result that an enormous amount has been written on the subject of coagulation. To review this mass of literature would only be repeating items already summarized in a number of modern books on Colloid Chemistry. Sufficient if, passing in review the most important experimental facts gleaned from the work of a great

---

[1] The substance of this article was included in a paper presented at the Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 27–28, 1927. A preliminary version was submitted for publication in THIS JOURNAL, October 10, 1927.

[2] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin, June, 1927. All work was carried out under the direction of Professors F. C. Krauskopf and J. H. Walton, to whom the author is deeply and gratefully indebted.

[3] Graham, J. Chem. *Soc.*, 15, 216 (1862); 17, 318 (1864).

many investigators, we mention four of the important current conclusions relating to coagulation. (1) Colloids may be coagulated by electrolytes, the ion of charge opposite to that of the colloid being the effective coagulant. (2) The coagulating power of an ion increases with the valency of that ion. (3) Each electrolyte appears to have a minimum concentration which must be reached before measurably rapid coagulation takes place.[4] (4) Coagulation is, in general, accompanied or preceded by adsorption of the coagulating ion.[5]

Even a cursory examination of the literature impresses one with the fact that there is great lack of agreement in the results upon which these and other conclusions are based. Due to the inherent nature of colloids and their apparent failure to conform to the laws which regulate the composition and behavior of pure compounds, we probably should not expect quantitative exactness in coagulation data, but a higher degree of accuracy and uniformity certainly is to be desired. Possibly the technique involved in making coagulation studies may be largely at fault. If so it should be intensely important to Colloid Science to correct this fault by substituting methods qualified to give more exact results.

If we inquire into the experimental technique employed by the numerous investigators in the field of coagulation, we find practical agreement in the methods employed. In most cases they have followed the general plan of adding varying amounts of the electrolyte in question to equal samples of the sol and noting the minimum amount required to bring about complete coagulation. The choice of electrolyte concentration seems to have been arbitrary, the only requirement being that it must be high enough to be capable of causing coagulation. Each worker has his own standardized concentration of sol and electrolyte and his own method of procedure. Some have used dilute sols, others concentrated. Some have added a concentrated solution of the electrolyte, others a rather dilute solution. The electrolyte has been added with stirring, without stirring, with agitation, without agitation, has been added rapidly and slowly. The time element has varied all the way from several minutes to several days. The decision as to the exact point of complete coagulation has, as a rule, rested on the appearance of the supernatant liquid obtained by centrifuging the treated sol, the absence of all color in the case of sols such as ferric oxide being taken as a positive index.

A combination of what seemed to him to be the best features of all past methods was employed by Ward[6] in connection with some unpublished

---

[4] Hatschek, "Introduction to the Chemistry and Physics of Colloids," P. Blakiston's Sons, Philadelphia, **1926,** p. 56.

[5] Weiser, "Colloid Symposium Monograph," 4, **354** (1926); Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., Inc., New York, 1926.

[6] Doctorate "Thesis," University of Wisconsin, 1926.

studies made at the University of Wisconsin. Although primarily intended as a coagulation study, Dr. Ward's work really developed into a critical examination of the accuracy of the method which he employed, and it is interesting to note that his conclusion was that the coagulation values obtained were "an estimate, in error by ten or twelve per cent." If technique of the caliber displayed by Dr. Ward and by others who have preceded him is capable of giving only an "estimate," in error by 10 or 12%, then apparently some improvement in the method of making coagulation studies is necessary, or at least desirable, if we are ever to learn the true mechanism of coagulation.

A possible course which an attempt at improvement might follow is suggested in the third and fourth of the previously listed conclusions relating to coagulation. The third states that "each electrolyte appears to have a minimum concentration which must be reached before measurably rapid coagulation takes place." Granting the truth of this statement, the incidence of rapid coagulation should be a function of electrolyte concentration. There should be a critical concentration at which noticeable coagulation should begin to take place instantly and throughout the entire sol. If we could gradually bring the electrolyte concentration up to this critical value the sol should then cloud and coagulate very suddenly. By accurately catching the value of this critical concentration we should, theoretically at least, have a method for determining what we might then call "critical coagulation concentration." Possibly the third conclusion is not entirely correct. Perhaps there is no such thing as a "stable" colloid. Stability may be only relative, the most "stable" colloid eventually undergoing complete coagulation without the assistance or intervention of any electrolyte. Still, since experimental evidence points to the fact that noticeable and measurably rapid coagulation is dependent upon the attainment of a minimum electrolyte concentration, any means of accurately catching the point at which this rapid rate becomes noticeable should be of value.

'She fourth conclusion suggests a method by means of which we could catch this point. If "coagulation is, in general, preceded or accompanied by adsorption of the coagulating ion," the concentration of the electrolyte should experience an abrupt decrease at the coagulation point. The extent of this decrease would depend upon the degree to which the coagulating ion is adsorbed. If there is such a decrease we should have little difficulty in observing it because we have methods for following changes in electrolyte concentration. In the case of ferric oxide sols the conductance method would seem to be the only acceptable one. Using this method we could simply plot time against resistance as we brought the electrolyte concentration up to the "critical" value. The break in the time–resistance curve would represent the critical point.

To catch the "critical point" would then appear to be a simple matter. The main problem is to be able gradually and uniformly to bring the electrolyte concentration up to the critical value without getting preliminary coagulation. We cannot add the electrolyte directly, as past investigators have done, because that would give us local coagulation. This local coagulation would gradually deplete the supply of colloid and we would finally end up with a completely coagulated sol without having experienced the desired break in our curve. Obviously we must start with an electrolyte concentration too low to cause even the most minute trace of local coagulation and gradually increase it uniformly by evaporation; or else we must allow the electrolyte to diffuse in through a membrane, uniformly, slowly and in such minute quantities as to prevent any local effects. In this way we would get volume coagulation, that is, coagulation throughout the entire sol. Perhaps it may seem that we are frustrated at the very outset because there is no such thing as perfect volume concentration of a sol. Neither can there be diffusion without differences in concentration. But we should be able to come very close to the ideal state and get almost if not quite perfect volume coagulation. That, after all, is the best that we can hope for in any method.

Experimental

Concentration by evaporation was first resorted to, potassium nitrate being the added electrolyte. Twenty-five cc. of sol was diluted with 25 cc. of $N/200$ potassium nitrate, the mixture placed in a conductance cell consisting of a 2.5 X 20 cm. test-tube in the bottom of which was sealed two platinized platinum electrodes and the latter immersed in a bath of boiling water. A current of dry air was blown over the surface of the sol. The resistance of the solution was taken at frequent intervals up to and beyond the coagulation point. The time-resistance curves obtained from three runs showed slight but very noticeable "breaks." The sol clouded sharply at the same time as the break occurred; this was followed very shortly by the appearance of floccules of coagulum. Some localized coagulation took place at the surface in each run. In order to eliminate this, prooision was made for stirring by bubbling clean air through the sol. The air bubbles caused coagulation, as did nitrogen, oxygen and hydrogen.[7] A pyrex stirrer was then used.

The evaporation method served its purpose in that it indicated that the desired "breaks" could be obtained and that values could be checked. However, it was abandoned as unsatisfactory because it was too slow and tedious, about eight hours of constant attention being required for each determination.

The method of increasing the concentration by allowing the electrolyte to diffuse in through a membrane was then resorted to. The conductance–diffusion cell (Fig. 1) consisted of two platinum electrodes, D, sealed into glass tubes which were firmly embedded in sealing wax contained in the space between the inner, K, and outer, J, collars. The outer collar was flanged out at the lower edge to facilitate attachment of the collodion bag. The inner collar, being open at both ends, permitted introduction of the pyrex stirrer, C. The electrodes were protected by four solid glass guard posts,

---

[7] A detailed study of the coagulation of sols by gas bubbles is now under way in this Laboratory.

G, which were embedded in the sealing wax. These posts extended a short distance below the lower edge of the electrodes and prevented their coming in contact with the collodion bag.

The collodion bag, B, was molded in an ordinary 3-cm. pyrex test-tube of convenient length. It was slipped over the flanged edge of the outer collar to the position shown and was held in place by a rubber band. Fifty cubic centimeters of sol, or sol-electrolyte mixture, was then introduced by means of a pipet, after which the cell was clamped in the position indicated in the figure and lowered into a beaker, **A**, containing electrolyte of the same concentration as that used in the preparation of the sol–electrolyte mixtures. By means of a simple constant-level device the level of the electrolyte in **A** was adjusted and maintained about equal to that of the sol in the bag, B. Beaker **A** was kept in a water thermostat bath at 25°, all determinations being made at this temperature. The motor-driven stirrers, C and C', which were started as soon as the cell had been lowered to its proper position, were operated at 220 and 400 r.p.m., respectively.

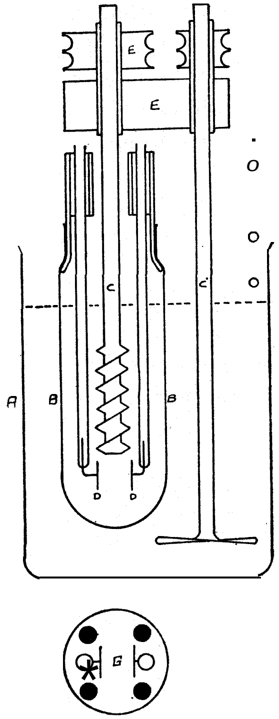


Fig. 1.

When the cell and its contents had come to the temperature of the thermostat, the desired electrolyte was introduced, drop by drop, at H from a water-jacketed buret whose temperature was kept constant at 25°. Time–resistance readings were then taken at frequent intervals until coagulation of the sol took place, the uniform drop-by-drop addition of electrolyte being continuously kept up. The location of the coagulation point was based on two criteria, the change in the appearance of the sol and the break in the time–resistance curve.

The break in the time–resistance curve having been properly located, the specific conductance corresponding to this break was calculated, and the electrolyte concentration corresponding to this specific conductance was read from an experimentally determined conductance–concentration curve. The final concentration was expressed in terms of normality and represented the critical coagulation concentration, that is, the concentration to which the electrolyte had to be raised before coagulation of the sol would take place.

The concentration of electrolyte run in at H was generally about ten times as great as that used in preparing the sol-electrolyte mixtures. The choice of this latter concentration was determined by elimination, a series of ranging concentrations being tried out and that one selected which just failed to show any signs of coagulation on twenty-four hours' standing.

The rate of addition of electrolyte at H was found to be important. If added too rapidly the high concentration gradient developed between the inside and outside of the membrane promoted such rapid diffusion into the sol that localized coagulation took place near the inner surface. Slower rate of addition was better since localized coagulation was then almost entirely avoided. However, regardless of how much care was exercised and how slowly diffusion took place, there was always some localized coagulation near the walls of the bag. Furthermore, the critical coagulation concentration was found to change with rate of addition of electrolyte, being greater with slow addition and less with rapid addition. When the rate of addition was kept constant, whether high, low or intermediate, results could be duplicated very closely.

The conductance–concentration curves from which the concentration of electrolyte at the "break" was read were drawn from values obtained from determinations made in aqueous solutions of the pure salts. Possibly it may seem that these curves should have been drawn from values obtained using ferric oxide sol as the diluent rather than conductivity water, but since we are interested in the effective electrolyte concentration at the coagulation point and not after coagulation has taken place, it is evident that the ordinary conductance–concentration curve is the one that should be used.

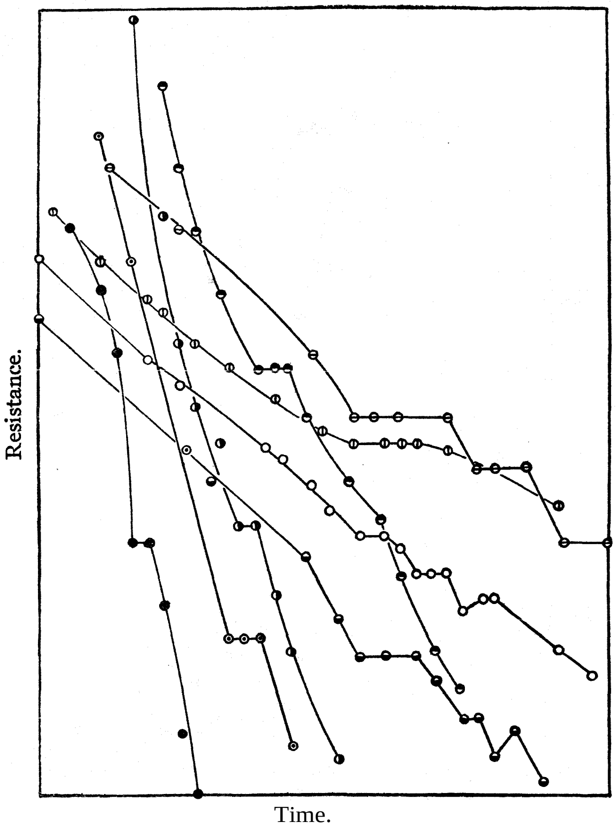
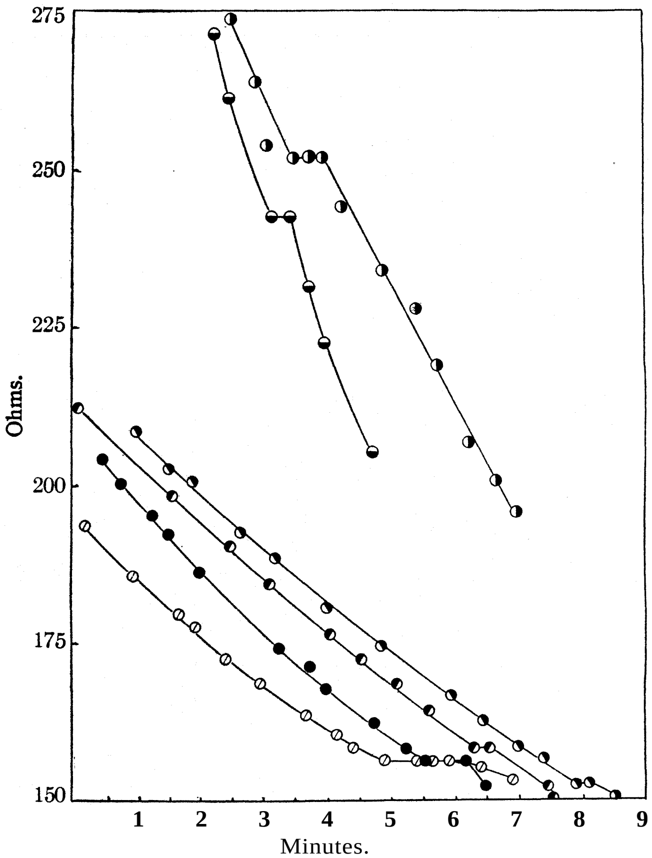


Fig. 2.

Coagulation studies were made with various electrolytes using various dilutions of sol. The particular sol employed was free from detectable amounts of chloride and was prepared in accordance with the method already described.[8] The iron content of the undiluted sol was 2.90 g. per liter.

Parts 1, 2, 3, 4, 5 and 6 of Table I show representative data obtained with six different electrolytes. Fig. 2 represents typical time–resistance curves, the resistance of the sol in ohms being plotted against time in minutes.[9] Parts 7 and 8, 9 and 10 and 11 and 12 of the table, with the corresponding curves (Fig. 3), show duplicate runs for potassium nitrate



Rapid addition: ◒, 7; ◑, 8. Slow addition: ●, 9; O, 10; ⊘, 11; ◔, 12.

Fig. 3.—Coagulation of ferric oxide by potassium nitrate.

---

[8] Sorum, This Journal, 50,1263 (1928).

[9] The conductance of the purified sol at 20° was found to be less than that of the conductivity water used in its preparation. This is in agreement with results described in a private communication from Dr. H. R. Kruyt, University of Utrecht, in whose laboratory purified sols with conductance lower than that of the water used in dialysis have been prepared.

TABLE I

REPRESENTATIVE DATA ON COAGULATION OF FERRIC OXIDE

1. By KNO_3

Time	Resistance
19:30	247
20.15	241
21:00	232
21:35	225
22:15	217
22:45	212
23:20	205
23.45	200
24:15	196
24:45	190
25:15	182
25:50	177
26:15	171
26:4.5	162
27:15	156
27:40	158
28:00	157
28:15	154
28:45	148
29:05	145

2. By KCl

Time	Resistance
11:36	104
12:45	91
13:30	83
14:00	78
14.30	75
14.45	74
15.00	74
15:30	74
15.45	74
16:08	73
16:18	72
16:45	71

3. By $K_3Fe(CN)_6$

Time	Resistance
149:00	13500
149:24	13100
150:15	12100
151:00	11400
151:30	11000
152:00	10800
152:36	10600
153:06	10100
153:45	9600
154:12	9400

4. By KBr

Time	Resistance
21:30	126
23:04	119
25:06	106
26:12	98
26:42	95
27:30	95
28 07	95
28:45	95
29.10	94
29:30	95
29:42	95
30:00	97

5. By K_2CrO_4

Time	Resistance
23:15	18400
29 30	16300
34:15	14800
45:15	11940
47:30	11440
49:30	11000
51:00	10500
52:00	10300

6. By $K_4Fe(CN)_6$

Time	Resistance
77:30	18000
84.45	16800
90:15	15700
94:15	13500
95:45	12400
96.45	11500
98:15	10000
99:15	9000

7. By KNO_3

Time	Resistance
13.16	324
13:30	320
14:00	292
14:18	272
14:32	262
14:52	256
15:08	243
15:25	243
15:45	232
16:05	223
16:22	218
16:45	206

KNO_3 0.01186 N at coagulation point

8. By KNO_3 (Duplicate)

Time	Resistance
16:40	313
17:00	$08
17:15	290
17:32	280
17:50	270
18:07	260
18:30	258
18.45	258
18:55	258
19:15	250
19:50	240
20:25	234
20.45	225
21:15	213
21:40	207
22 00	202

KNO_3 0.01135 N at coagulation point

9. By KNO_3

Time	Resistance
14:15	174
15:00	167
15:15	165
15 45	162
16:12	158
16:35	156
17:10	156
17:30	152
18:15	147
19:50	140

KNO_3 0.0154 N at coagulation point

10. By KNO_3 (Duplicate)

Time	Resistance
10:30	172
10:50	170
11:05	168
11:25	166
11:40	164
11:45	163
12:00	161
12:15	160
12:30	158
13:00	156
13:30	156
13:45	156
14:00	156
14:30	155
15:00	153
16:15	146

KNO_3 0.0154 N at coagulation point

11. By KNO_3

Time	Resistance
12:00	161
12:21	160
12:36	159
13:06	157
13:24	156
13:45	154
14:00	154
14:21	152
14:50	151
15:00	150
15:35	148
16:00	147

KNO_3 0.01906 N at coagulation point

12. By KNO_3 (Duplicate)

Time	Resistance
13:48	162
15:38	160
16:00	158
16:32	156
17:06	154
17:26	153
17:55	151
18:20	151
18:40	150
19:00	149
19:15	148
19:36	147

KNO_3 0.01973 N at coagulation point

with a sample of sol whose iron content was 1.45 g. per liter. These latter curves emphasize the fact that the critical coagulation concentration changes with rate of addition of electrolyte, being greater with slow addition and less with rapid addition. They show, further, that results can be duplicated quite closely when the rate of addition is kept reasonably constant.

Discussion

Since there is no standard by which the accuracy or inaccuracy of any method of making coagulation studies can be correctly judged, one cannot say that the conductance–diffusion method as outlined is capable of either greater or less accuracy than the classical method used by past investigators. Certainly the conductance–diffusion method does not give quantitative values, but when a standardized method of procedure is used results can be duplicated very accurately. The personal factor is largely eliminated since the location of the critical coagulation point is determined by the change in the course of a time–resistance curve.

The "break" in the time–resistance curve is an experimental fact, as the graphs will show. It was assumed at the outset that this "break" was due to the adsorption of electrolyte during coagulation. Such may or may not be the case. Perhaps the voluminous coagulation at the critical point impairs free diffusion, thereby creating a break in the curve. The fact that the majority of "breaks" are "plateaus" lends support to this view. The irregularities in the course of the curve following the first "break" lend further support, uniform diffusion of the electrolyte being impossible in the presence of a large volume of coagulum. This interference with free diffusion may also be the cause of the successive "breaks" that are to be observed in some of the curves.

Further study of the conductance–diffusion method is now under way in this Laboratory.

Summary

1. A conductance–diffusion method for studying the coagulation of colloidal ferric oxide by electrolytes has been described.
2. Data are presented to show the application of the method.

MADISON, WISCONSIN

NOTES

Dissociation and the Color of Free Radicals.—M. Gomberg and F. W. Sullivan, Jr.,[1] have determined the depression in freezing point caused by dissolving diphenyl-β-naphthylmethyl in the three solvents, benzene, nitrobenzene and cyclohexane, at various concentrations and have paralleled these measurements with colorimetric examinations of the same solutions. They observed that the deviation from Beer's law exhibited by these solutions was not proportional to the dissociation as measured by cryoscopic methods and decided that the color could not be due to simple dissociation of tetraphenyldi-β-naphthylethane. They concluded[2] that "the observed facts can best be explained by the assumption that we are dealing here with an equilibrium between benzenoid and quinonoid tautomers of the triarylmethyl, and that an increase in the proportion of the quinonoid tautomer (upon dilution) is the cause of the increase of color."

This conclusion is incompatible with the evidence upon which it is based, for such an increase in the proportion of the quinonoid tautomer could not occur in a system obeying the law of ideal dilute solutions which was implicitly assumed in calculating the degree of dissociation. In such a system the mass action law has a rigid thermodynamic basis and for a simple tautomeric equilibrium between two molecular species

$$C/C' = K \tag{1}$$

that is, the ratio of the equilibrium concentrations of the two tautomers is independent of the total concentration for an ideal solution. Gomberg and Sullivan necessarily assumed their solutions to be ideal in order to calculate the degree of dissociation from cryoscopic measurements. Therefore, if their calculations were valid, the tautomeric equilibrium constant could not vary upon dilution. Of course, this variation is possible in a real solution which need not behave ideally, but their calculations are not applicable to such a solution. Thus, the degree of dissociation, calculated from cryoscopic measurements by any known methods, *cannot possibly furnish any basis* for the conclusion that the equilibrium constant of a tautomeric process varies with dilution.

It is now pertinent to inquire what conclusions, if any, may be drawn from these measurements of Gomberg and Sullivan. The congruence of the cryoscopic data can be tested independently by calculating the equilibrium constant for a binary dissociation. This has been done by Walden,[3] who found that a satisfactory constant did not result. These cryoscopic measurements, therefore, do not give correct values for the dissociation of the ethane and, consequently, *they do not furnish a reliable basis for comparison with the colorimetric data.*

[1] Gomberg and Sullivan, THIS JOURNAL, 44, 1810–1833 (1922).

[2] Ref. 1, p. 1832, lines 18–22.

[3] Walden, "Chemie der freien Radikale," Leipzig, 1924, pp 200, 294 297

It is possible to test the colorimetric measurements, independently, to determine whether or not the dissociation and color are proportional, provided these measurements are sufficiently accurate. The law of mass action for a binary dissociation may be expressed.[4]

$$K = C\alpha^2/(1 - \alpha) \tag{2}$$

in which C is the molal concentration, α is the degree of dissociation and K is a constant. When the dissociation is proportional to the intensity of color (H)

$$\alpha = IH \tag{3}$$

and

$$K = CI^2H^2/(1 - IH) \tag{4}$$

The condition that K shall actually remain constant for two sets of experimental values, C_1, H_1 and C_2, H_2, is clearly

$$C_1I^2H_1^2/(1 - IH_1) = C_2I^2H_2^2/(1 - IH_2) \tag{5}$$

and the unique value of **I** which can satisfy this condition for any pair of measurements is given by

$$I = (C_1H_1^2 - C_2H_2^2)/(C_1H_1^2H_2 - C_2H_2^2H_1) \tag{6}$$

The values of **I** X 10^2 have been calculated from the data of Gomberg and Sullivan[5] and appear in Table I, where the values given under H represent the intensity of color in mm. of standard solution and those under V are the volumes of the solutions employed. These investigators made up their solutions by dissolving 0.25 g. of the substance in 5 cc. of solvent and then diluting to 10 cc. and 23 cc., respectively. Since the value of **I** is related to the ratio of the concentrations and is independent of their absolute value, the simple numbers 1, 0.5 and 0.2 may be substituted for C_1 and C_2 in Equation 6. Accordingly, the absolute values of C are not recorded in the table.

Table I

Dissociation and the Color of Diphenyl-β-naphthylmethyl

	Nitrobenzene		Benzene		Cyclohexane	
V	H	I X 10^2	H	I X 10^2	H	I X 10^2
5	13	2.5	11.5	0.6	10	0.5
10	17		16		14	
25	25	1.3	23	1.8	19	3.0

It is apparent from these values that Equation 3 is not established by the data. However, it is not disproved, either, for the values of H may obviously be in error by as much as 0.5 mm. By substituting 10.5 and 13.5 for the first two values of H in cyclohexane, for instance, the value 0.036 instead of 0.005 is obtained for **I**. Thus the large variations in the table are within the limits of accuracy of the colorimetric measurements."

---

[4] Nernst, "Theoretical Chemistry," 5th Eng. ed., London, 1923, p. 589.

[5] Ref. *1*, p. 1827.

[6] *In* fact, by choosing an optimum value of I from the table, much more satisfactory values of K are obtained than are furnished by the cryoscopic measurements

It follows, therefore, that *these measurements are not sufficiently accurate to test thoroughly the relation between the color and dissociation.*

CONTRIBUTION FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 219
CAMBRIDGE, MASSACHUSETTS
CHARLES BUSHNELL WOOSTER[7]

RECEIVED JULY 16, 1928
PUBLISHED APRIL 5, 1929

The Confirmatory Test for Aluminum.—As a result of experiments carried out in this Laboratory last year, we were about to publish an account of a modified test for aluminum when a published account of practically the same test appeared.[1] Our procedure for carrying out the test was as follows. Pure asbestos fiber, one-half the size of a pea, was looped in a platinum wire, dipped into a solution of 0.05 N cobalt nitrate, ignited, then dipped into the solution of the aluminum hydroxide precipitate (dissolved in the least amount of nitric acid) and ignited.[2] We found that the test was easily sensitive to 0.2 mg. of aluminum, that the sodium salts did not interfere and that there was no danger of losing the test as with the fragile filter paper ash. This modified procedure is now being used successfully in our classes. Furthermore, we found that this procedure could he used for zinc, 0.5 mg. of the metal being detected with ease.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK
RAYMOND GEMMILL
ROBERT BRACKETT
C. R. MCCROSKY

RECEIVED NOVEMBER 24, 1928
PUBLISHED APRIL 5, 1929

A Method for Determining Vapor Densities at Room Temperatures.—A summary of various methods for determining vapor densities is given by Biltz,[1] Windisch[2] and Arndt.[3] A method differing somewhat from any of these was developed and tried out to some extent. It can be carried out at room temperature and the apparatus can easily be built from parts found in any chemical laboratory.

Two two-liter round-bottomed flasks are connected by an oil manometer made of glass tubing of 5-mm. inside diameter. Means for evacuating the flasks simultaneously is provided by two stopcocks joined by a

[7] National Research Fellow.

[1] Paiiganiban and Soliven, THIS JOURNAL, 50, 2427 (1928).

[2] A. A. Noyes, "Qualitative Chemical Analysis," p 190.

[1] Biltz, "Practical Methods for Determining Molecular Weights," The Chemical Publishing Company, 1899.

[2] Windisch, "Bestimmung des Molekulargewichts," Julius Springer, Berlin, 1899.

[3] Kurt Arndt, "Handbuch der physikalisch-chemischen Technik," Ferdinandt Enke, Stuttgart, 1923.

glass tee and connected through a mercury manometer to a vacuum pump, which may be an ordinary aspirator. The liquid whose vapor density or molecular weight is to be' determined is sealed up in an ordinary Victor Meyer vapor density bulb and hung in a loop formed by one end of a stiff copper wire coil wrapped around the sealed end of the oil manometer, projecting four inches into the flask. A small hole is blown in the manometer tubing just below the rubber stopper. The flasks are now evacuated to about one centimeter of mercury pressure and the stopcocks closed. The bulb containing the liquid is crushed against the manometer tubing by an angle bent at the end of the stem of the stopcock, which can be turned from outside. In a few minutes, when the liquid has evaporated and equilibrium conditions have been reached, the increase in pressure indicated by the manometer is observed. This amounts to about 29 centimeters of oil when 0.1 g. of ethyl alcohol is used.

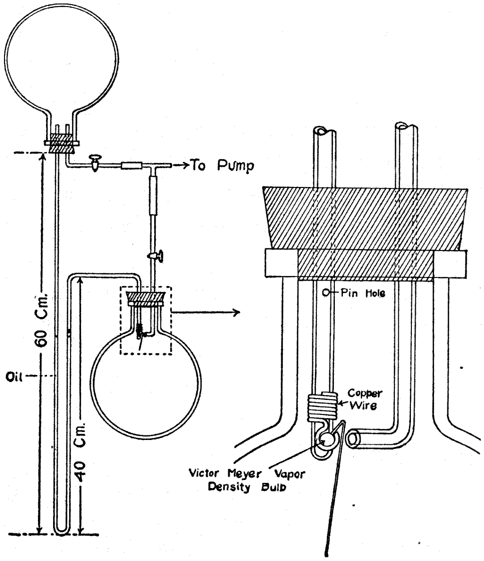


Fig. 1.

The temperature can be determined by a thermometer hung inside or near the flask. The volume of the flask, which must be determined, is made more uniform for different determinations by grinding a shoulder on a rubber stopper that is much too large at first. All the quantities in the familiar gas equation, $PV = WRT/M$, are known except M, which can be calculated.

The error in the pressure reading due to the decrease in volume in the upper flask and increase in the lower flask totals on the average 0.2 mm. of oil and may be neglected. The main precaution to be observed is not to warm the flask with the hands.

The approximate minimum vapor pressure which the substance exerts at room temperature should be 4 cm. of mercury or more. For substances of lower vapor pressure or small molecular weight, a small sample, a larger flask or higher temperatures would be required.

Of the data thus far obtained may be mentioned those taken by Trepp[4] for benzene, 79.7, 79.38, 81.0, 79.13, 79.64, 80.19, 79.42 and 80.23 and for ethyl alcohol 45.34, 44.30, 45.86, 45.99, 45.53, 45.48, 45.29 and 45.34.

[4] Senior Student, University of Michigan.

These determinations were made at 23–26°. The benzene was of high purity. The average value obtained for the sample of alcohol corresponded closely to that obtained for it by the Victor Meyer method.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

ERWIN F. LINHORST[5]

RECEIVED DECEMBER 6, 1928
PUBLISHED APRIL 5, 1929

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

DOUBLE SALTS OF ANILINE HYDROHALIDES WITH METAL HALIDES

BY GORDON D. BYRKIT AND WILLIAM M. DEHN

RECEIVED AUGUST 1, 1928 PUBLISHED APRIL 5, 1929

Aniline reacts in a great variety of ways with metallic salts to form molecular compounds, to yield oxidized and halogenated derivatives and to substitute amino or nuclear hydrogen by metal or metal–halide groups.[1] The object of this study is to review and extend the knowledge of molecular compounds of the types $n\text{An}\cdot n\text{HX}\cdot\text{MX}_n$, wherein An is aniline, X is halogen and M is metal. These and their hydrated forms are assembled in the following table. The asterisk indicates new compounds herewith contributed. The symbol of the metal is followed by its valence only where it is other than of the "ic" salt. The types of salts are arranged in the order of increasing complexity with respect to aniline hydrohalide. It will be noted that anhydrous salts are only numbered, while hydrated salts are lettered and correspondingly numbered. There are nine degrees of complexity of anhydrous salts and eight of hydrated salts, making seventeen types of complexity with respect to both aniline hydrohalide and water. In the absence of molecular weight determinations, the simplest formulas are used in the table. There is no evidence that these salts are not polymerized. For example, $\text{AnHCl}\cdot\text{HgCl}_2$ may be $(\text{AnHCl}\cdot\text{HgCl}_2)_x$.

Many of the compounds indicated by the blanks of the table were sought but could not be prepared. The known compounds, therefore, because they are most easily formed, roughly represent comparative capacities of the different metals to unite with aniline hydrohalide, their limits of capacity to enter into such union and the relative affinities of the three halogens.

As is shown in its greater number of types and its ability to form the ***octo-aniline*** compound, it is concluded that mercury has the greatest

---

[5] Graduate Student, University of Michigan.

[1] See especially Whitmore's "Organic Compounds of Mercury," Chemical Catalog Company, New York, 1921, p. 205.

TABLE I

ANHYDROUS AND HYDRATED DOUBLE SALTS

		Metals forming such salts where X is									
		Chlorine				Bromine				Iodine	
Type	Formula	M	Lit.	M	Lit	M	Lit.	M	Lit	M	**Lit**
1	$AnHX\cdot 2Mx_n$	Hg	1			Hg	*			...	
2	$AnHX\cdot MX_n$	Hg	1	Mn	*	Cu^1	4	Cd	17	Hg	*
				Bi	*					Sb^3	2
						Sn^2	6	Al	18	Bi^3	23
2a	$AnHX\cdot MX_n\cdot H_2O$	Sb^3	2	Sn^2	3						
3	$4AnHX\cdot 3MX_n$					...				Pb	24
4	$3AnHX\cdot 2MX_n$	...				Al	17			Sb^3	2
5	$2AnHX\cdot MX_n$	Co	*	Sn	7	Sb^3	2	Zn	11	Zn	11
		Au	*	Fe	8	Cu^1	4	Al	18	Cd	11
		Hg	1	Te	9	Sn	6	Cd	20		
		Cu^1	4	Zn	10	Te	19	Pt	21		
		Cu	5	Cd	11						
		Sn^2	3,6	Pt	12						
5a	$2AnHX\cdot MX_n\cdot H_2O$	Fe	13	Zn	14	Zn	14			...	
5b	$2AnHX\cdot MX_n\cdot 2H_2O$	Mn	*	Fe^2	13	...				...	
				Fe	13						
5c	$2AnHX\cdot MX_n\cdot 3H_2O$	Sn	7			..				...	
6	$3AnHX\cdot MX_n$	Al	*	Bi^3	15	As	*				
		Sn	*								
6a	$3AnHX\cdot MX_n\cdot H_2O$	Sb^3	2			..				..	
6b	$3AnHX\cdot MX_n\cdot 2H_2O$	Zn	14							...	
7	$4AnHX\cdot MX_n$	Sn	6	Fe	16	Sb	2	Al	18	Sb^3	**2**
						Sn	6	Te	22		
7a	$4AnHX\cdot MX_n\cdot H_2O$	...				Sb^3	2			..	
8	$6AnHX\cdot MX_n$	Fe	13							..	
8b	$6AnHX\cdot MX_n\cdot 2H_2O$	Fe	13			..				...	
9	$8AnHX\cdot MX_n$	Hg	*			..				...	

(1) Swan, *Am. Chem.* **J.**, 20, 613 (1898); Frank C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Company, New York, 1921, pp. 205–210, 374; (2) Higbee, *Am. Ckem.* **J.**, 23, 154 (1900); (3) Slagle, *ibid.*, 20, 663 (1898); (4) Saglier, *Compt. rend.*, 106, 1422 (1888); (5) Destrem, *Bull. soc. chim.*, 30, 482 (1878); (6) Richardson and Adams, *Am. Ckem.* **J.**, 22, 446 (1899); (7) Slagle, (3); Druce, *Chem. News*, 117, 346 (1918); (8) McKenzie, *Am. Chem.* **J.**, 50, 308 (1913); Osaka, Schima and Soshida, *Mem. Coll. Sci., Kyoto Imp. Univ.*, 7, 69 (1924); (9) Lenher, THIS JOURNAL, 22, 139 (1900); (10) Tombeck, *Ann. chim.*, [7] 21, 433 (1900); Vohl, *Dingler's polyteck.* **J.**, 175, 211 (1865); (11) Tombeck, (10); (12) Hofmann, *Ann.*, 47, 62 (1843); (13) McKenzie, (8); (14) Base, *Am. Chem.* **J.**, 20, 646 (1898); (15) Hauser and Vanino, *Ber.*, 33, 2271 (1900); (16) Osaka, Schima and Soshida, (8); (17) Hjortdahl, *Z. Krist*, 6, 484 (1882); (18) Kablukov and Knanov, **J.** *Russ. Phys.-Chem. Soc.*, 41, 1755 (1910); (19) Lenher, (9); Lowy and Dunbrook, THIS JOURNAL, 44, 614 (1922); (20) Tombeck, (10); Hjortdahl, (17); (21) Gutbier, *Ber.*, 43, 3228 (1910); (22) Lowy and Dunbrook, (19).

capacity of all the metals to enter into such molecular combinations.[2] Ferric halide seems to approach mercury in this respect, and other metals

---

[2] This was observed also with the quinoline compounds, THIS JOURNAL, 48, 275 (1926); 48, 277 (1926).

in the order of lesser capacity seem to be tin, zinc and antimony. Chlorine seems to favor the greatest complexity; however, with quinoline, bromine was found to yield the greatest complexity. Iron, antimony and zinc are the most capable of forming hydrated salts with aniline hydrohalides: the bromides rarely form hydrated salts with aniline hydrohalides; the bromides rarely form hydrated salts; the iodides form none. Though magnesium bromide unites with 2, 4 and 6 moles of aniline, it could not be made to unite with aniline hydrobromide, either in hydrobromic acid or methylethyl ketone solutions.

Efforts to correlate these properties have in the past led to no certain conclusion, nor does it seem possible today to make any definite correlation.

All these compounds are double salts rather than complex salts, because they precipitate all of their halogen with silver nitrate, they liberate all of their metal with hydrogen sulfide or sulfuric acid and all of their aniline with sodium hydroxide or sodium carbonate.

That Werner's theory is inadequate to explain the constitution of these compounds[3] is especially evidenced by the existence of the iron-hexaniline compound and the octo-aniline compound of mercury. Furthermore, compounds of the table show no properties of the "inner zone."

In the preparation of heavy metal salts of the alkaloids and other bases for analytical purposes, it is usually assumed that the composition of the precipitate corresponds to Type 2, Base $HX\cdot MX_n$. That this assumption may lead to error is sufficiently indicated by this study, wherein it is especially shown that metals exercise a wide capacity to form salts of different types, under various conditions of solvent concentration, etc.

Experimental Part

In the preparation of these compounds, 0.08 mole of aniline hydrohalide and 0.01 mole of metal halide were weighed out, dissolved in the minimum amount of hot alcohol, methylethyl ketone or concentrated hydrohalogen acid, filtered and allowed to cool to room temperature. If no crystals formed, the solution was allowed to cool in a freezing mixture or the solvent evaporated spontaneously. Crystals formed were filtered out and washed with a small amount of the solvent from which they precipitated except that when too soluble the use of ether or benzene was found more satisfactory for washing. When the crystals appeared homogeneous and microscopically different from the original materials they were analyzed for metal, usually by precipitation of the sulfide. If the crystals were aniline hydrohalide or metal halide, they were re-

---

[3] Recent work with other bases also shows the inadequacy of Werner's theory [Scagliarini and Monti, *Atti Accad. Lincei,* [6] **1,** 582 (1925), [6] 2, 269 (1925); [A] **4,** 210 (1926)].

turned to the solution from which they precipitated, 0.01 mole of metal halide was added (with more solvent if necessary), the solution filtered and again allowed to crystallize. In case the double salt $4AnHX{\cdot}MX_n$ also failed to form, another 0.01 mole of metal halide was added and so on. If at any time a salt in other proportions was indicated, as, for example, Type **3**, an attempt was made to prepare it directly with the calculated quantities of material.

Often the expected salt did not form but one containing proportionately less aniline hydrohalide appeared. In cases of this kind the addition of a slight excess of aniline hydrohalide or of aniline over the theoretical quantity favored the formation of the more complex double salt.

The solvent used often had a marked effect on the complexity of the double salt formed. For example, when aniline hydrochloride and cobalt chloride were dissolved in concentrated hydrochloric acid, only aniline hydrochloride precipitated, but in methylethyl ketone $2AnHCl{\cdot}CoCl_2$ was formed.

Complex types tend to decompose to more simple types with rising temperature. This was found noticeable both in preparing the salts and in determining their melting points. Thus $2An{\cdot}HgCl_2$ softens at

TABLE II

DOUBLE SALTS OF ANILINE

Composition, An = $C_6H_5NH_2$	Color, etc.	Crystal form	Softens, °C.	M. p., °C.	M, % Calcd.	M, % Found
$8AnHCl{\cdot}HgCl_2$	White	Needles	...	231.5	15.34[a]	15.42[a]
$3An{\cdot}HCl{\cdot}2HgCl_2$	Glistening	Needles[b]	160	167	46.41	46.40
$AnHBr{\cdot}2HgBr_2$	Colorless	Plates	...	156	44.83	45.11
$AnHI{\cdot}HgI_2$	Yellow	......	...	61	29.70	30.17
$2AnHCl{\cdot}CoCl_2$	Blue	......	...	135	15.16	15.48
$2AnHCl{\cdot}AuCl_3$	Golden	Prisms[c]	85	95	35.49	35.40
$AnHCl{\cdot}BiCl_3$	White	Rectangles	210 (d.)	...	45.23	44.97
$AnHCl{\cdot}MnCl_2$	White	Needles	...	...	21.51	20.60
$2AnHCl{\cdot}MnCl_2{\cdot}2H_2O$	White	Needles	...	230+	13.05	13.13
$3AnHCl{\cdot}AlCl_3$	White	Rectangles[d]	...	...	5.19	5.29
$3AnHCl{\cdot}SnCl_4$	White	Needles	...	...	18.20	18.65
$3AnHBr{\cdot}AsBi_3$	White	Powder	...	...	8.95	8.88
$An{\cdot}HgBr_2$	White	......	...	127	44.23	44.43
$An{\cdot}PbCl_2$	White	Needles[e]	...	...	55.82	56.13

[a] X, calcd., 27.11. Found: X, 27.08.

[b] Prepared in hot alcohol.

[c] On heating the hydrochloric acid solution of this salt the solution darkens and precipitates pure gold in fern-like aggregates of short prisms. The reaction appears to be similar to that observed in the case of $2An{\cdot}HgI_2$. In each the metal halide is reduced and presumably the aniline is oxidized.

[d] Prepared in a large volume of hydrochloric acid with an excess of 2 moles of aniline.

[e] Mandal, Ber., 54, 703 (1921), gives a salt, $3An{\cdot}PbCl_2$, needles easily decomposed at 20–30° or by organic solvents.

about 130° with apparent loss of aniline and the formation of $An \cdot HgCl_2$, which then melts at 188°. In the preparation of the more complex types, the constituents were best dissolved in the minimum amount of solvent at room temperature and cooled in a freezing mixture.

Summary

Aniline exhibits a wide capacity to form compounds in combination with halogen and different metals. Seventeen types, including hydrated forms, are recognized. No correlation with properties can be made of all of these compounds on the basis of modern theories. The octo-aniline compound of mercury is easily prepared and is of special interest.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE LABORATORY OF PHARMACOLOGY, THE UNIVERSITY OF CHICAGO, AND THE DEPARTMENT OF MATERIA MEDICA AND THERAPEUTICS, THE MEDICAL SCHOOL, THE UNIVERSITY OF MICHIGAN]

A METHOD FOR THE QUANTITATIVE DETERMINATION OF CYANIDE IN SMALL AMOUNTS

BY RALPH G. SMITH[1]

RECEIVED AUGUST 10, 1928 PUBLISHED APRIL 5, 1929

The following method is the application of an established reaction in organic chemistry for the quantitative estimation of cyanide in small amounts. The method depends on the development of a reddish-brown color due to the formation of the sodium or potassium salt of isopurpuric acid, which occurs when cyanide is added to an alkaline picrate solution. In the presence of an excess of alkaline picrate the development of the color is quantitative, making it possible to estimate the amount of cyanide present colorimetrically by comparison with a standard prepared with a known amount of cyanide.

Durien[2] applied such a method for the quantitative estimation of hydrocyanic acid in bitter almond water. Runne,[3] in a survey of the quantitative methods for the determination of cyanide, established the procedure of Durien as accurate to within one per cent. Waller[4] used a similar method in the analysis of tissue distillates for hydrocyanic acid. From a stock solution of alkaline picrate containing a definite amount of cyanide, color standards are prepared with which the unknown solution is compared. Furthermore, as Waller has pointed out, the reaction has been described previously as a qualitative test for cyanide, by various workers.[5]

---

[1] Fellow in Medicine of the National Research Council.

[2] Durien, *Jahresb. Pharm.*, 37, 439 (1902).

[3] Runne, *Apoth.-Ztg.*, 24, 357 (1909).

[4] Waller, *J. Physiol.*, 40 (Proceedings of the Physiological Society, June 18) (1910).

[5] Hlasiwetz, *Ann.*, 110, 289 (1859); Reichardt, *Chem.-Ztg.*, 25, 537 (1901); Guignard, *Ann. sci. pharmacol.*, 415 (1906).

However, since the method has been developed in a somewhat different manner and as some of its possibilities and limitations have been examined, it is considered to be of sufficient interest to report.

The details of the method which have been found to give satisfactory results are as follows. Into a test-tube with a 25-cc. graduation are pipetted *3* cc. of saturated picric acid solution, *1* cc. of *5%* sodium carbonate solution (which ensures an alkaline reaction) and *1* cc. of the cyanide solution to be determined. The tube is heated in a boiling water-bath for five minutes, then cooled in running water and the volume made up to *25* cc. The solution is then compared in a colorimeter with a standard prepared in an identical manner. The amount of cyanide which has been found satisfactory for the standard is *1* cc. of *N*/500 potassium or sodium cyanide, a depth of solution of *20* mm. being used in the colorimeter.

Using such a procedure Table I shows the results of a series of determinations of solutions of sodium cyanide of various concentrations. All solutions were prepared from the same stock solution (*N*/10 sodium cyanide) to avoid errors due to standardization. The results demonstrate the determination of sodium cyanide in amounts of the order of *0.1* mg. within 1% error.

TABLE I

QUANTITATIVE DETERMINATION OF SODIUM CYANIDE SOLUTIONS

Standard contained *1* cc. of *N*/500 sodium cyanide soln. (*0.0980* mg. of NaCN)

1 *cc.* of *N*/600 soln. (0.0817 mg. of NaCN)		**1 *cc.* of *N*/550 soln. (0.0891 mg. of NaCN)**		**1 *cc.* of *N*/450 soln. (0.1088 mg. of NaCN)**		**1 *cc.* of *N*/400 soln. (0.1225 mg. of NaCN)**	
Col. reading, mm.	**Amt. detd., mg.**	**Col. readina, mm.**	**Amt. detd., mg.**	**Col. reading, mm.**	**Amt. detd., mg.**	**Col. reading, mm.**	**Amt. detd., mg.**
24.1	*0.0813*	*22.1*	*0.0887*	*18.0*	*0.1088*	*15.9*	*0.1233*
23.9	.0820	*22.0*	.0891	*18.0*	.1088	*16.1*	.1217
24.0	.0817	*22.0*	.0891	*18.2*	.1077	*15.9*	.1233
24.0	.0817	*22.2*	.0883	*17.9*	.1094	*15.9*	.1233
24.0	.0817	*22.2*	.0883	*18.2*	.1077	*18.0*	.1225

In the boiling water-bath the color develops rapidly, about 90% of the intensity being present in two minutes. It gradually increases up to five or six minutes' heating and then fades slightly on further heating. After ten minutes in the water-bath there is a slight but definite decrease in the intensity and after twenty minutes this decrease amounts to approximately 5%. On heating for one hour the decrease in intensity approaches *20%.*

Although the color developed by heating on a water-bath for five minutes is approximately 90% of the intensity obtained by boiling to a small volume over an open flame, it has been arbitrarily adopted in the method as the procedure is more convenient, especially if a number of determinations are to be made. Moreover, it is permissible in that constant results are given. At room temperature the color becomes apparent within one minute after the addition of the cyanide to the alkaline picrate solution. It develops comparatively rapidly at first, reaching *50%* of its intensity in from one-half to one hour after the addition of the cyanide. It attains its maximum only after standing from twenty-four to forty-eight hours.

The color developed has been found to be permanent for at least one month.

A consideration which is of importance is the fact that a picric acid solution alkalinized with sodium hydroxide yields a reddish-brown color even in the absence of cyanide, the intensity of the color varying with the concentration of the alkali. Moreover, the intensity of the color developed by cyanide is decreased in the presence of sodium hydroxide. This appears to be rather a serious obstacle in that cyanide distillates are commonly collected in a solution of sodium or potassium hydroxide. However, such solutions neutralized with hydrochloric acid yield accurate results, so the difficulty may be obviated in this manner. In the presence of an appreciable quantity of the potassium ion there is a precipitation of potassium picrate due to the low solubility of that salt. However, on heating it is redissolved and remains in solution on diluting to the 25-cc. volume.

In the application of the method it must be remembered that the presence of certain reducing substances which cause the formation of a reddish color in alkaline picrate solutions will interfere with the validity of the test. Among these are sulfides, hydrosulfites, aldehydes and ketones, including the reducing sugars. However, these substances must be present in a concentration of a much higher order than that of cyanide before they become a factor. A number of compounds have been tested with a view to gaining some idea of this relationship. Table 11 shows the concentrations of the various substances necessary to produce a color of an intensity comparable with that of the standard when 1 cc. of the solution is used in the test according to the above procedure. It is evident from these results that in order to be a factor such substances must be present in very appreciable quantities. The possibility of obtaining furfural or its derivatives in tissue distillates was considered. On boiling liver and muscle tissue in 2% tartaric acid solution, a qualitative alkaline picrate test on the distillate was negative. In order to subject to a more crucial test the possibility of the formation of furfural compounds by the action of tartaric acid on carbohydrates, the following experiment was made. Gum arabic, a pentose which is more readily decomposed by acids than are hexoses, was boiled in 10% tartaric acid, a concentration much greater than that necessary for distilling cyanide from tissues.[6] The distillate gave a negative alkaline picrate test and a very faintly positive Molisch test. Consequently it was concluded that furfural compounds would not be an interfering factor in tissue distillates.

TABLE II

RESULTS OF TESTS

Substance	%	Substance	%[a]
Standard (potassium cyanide)	0.011	Formaldehyde (40%)	Color too pale to compare
Ammonium sulfide	0.4	Acetoacetic ester	
Dextrose	0.4	Ethyl acetate	No color developed
Acetaldehyde	15.0	Ethyl alcohol	
Acetone	20.0	Methyl alcohol	
Furfural	10–15	Acetic acid	

[a] Percentage of substance necessary to give color comparable with the standard.

---

[6] Bischoff, *Ber.*, 16, 1351 (1883).

Used qualitatively the test is very sensitive. By looking through the depth of a test-tube of solution against a white background and comparing with a control tube of alkaline picrate solution, the detection of very small amounts of cyanide is made possible. In the 25-cc. volume used in the test one in ten million (CN) is very easily distinguished, one in twenty million (CN) is quite distinct and one in fifty million is distinguished definitely but with more difficulty.

I wish to thank Dr. A. L. Tatum for the suggestion and direction of this research.

Summary

1. A method for the quantitative determination of cyanide in amounts of the order of 0.1 mg. within 1% error is described. The method depends on the formation of a reddish-brown color which occurs when cyanide is added to an alkaline picrate solution.

2. The effects of time and temperature on the development of the color are discussed.

3. The presence of certain reducing substances which cause the development of a red color in alkaline picrate solutions may invalidate the method. The concentration of such substances necessary to be an interfering factor is indicated.

4. Used qualitatively the test is sensitive to one part of cyanide (CN) in fifty million.

CHICAGO, ILLINOIS, AND ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE WALKER CHEMICAL LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

THE FORMATION OF PYRROLINES FROM GAMMA-CHLOROPROPYL AND CYCLOPROPYL KETIMINES[1]

BY JOHN B. CLOKE

RECEIVED AUGUST 24, 1928 PUBLISHED APRIL 5, 1929

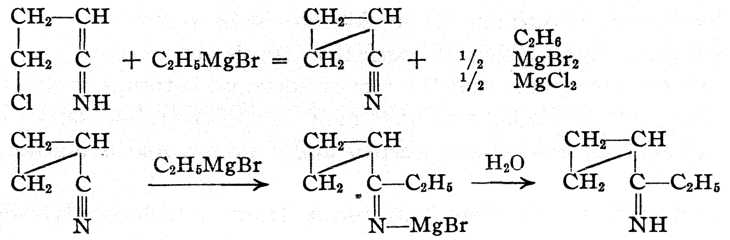
In a long, interesting paper appearing in 1923 de Booseré[2] reported the isolation of ethyl cyclopropyl ketimine and its hydrochloride with several other products following the action of magnesium ethyl bromide on γ-chlorobutyronitrile. The mechanism indicated by him for the origin of the ketimine follows closely an earlier one formulated by Bruylants[3] for an entirely analogous reaction. The equations follow.

---

[1] This paper is constructed from the first part of a dissertation to be presented by John B. Cloke to the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] De Booseré, *Bull. soc. chim. belg.*, 32, 2651 (1923).

[3] Bruylants, *Bull. sci. acad. roy. belg.*, **12**, 1082–1084 (1908).



Ketimines react normally with water to give the corresponding ketone and ammonia, as follows: $R—C(=NH)—R' + H_2O = R—CO—R' + NH_3$. Ordinarily this change is greatly accelerated by acids. Until de Booseré's paper appeared, qualitative reports concerning the rate of this reaction, notably by Mignonac,[4] indicated that it increases as the substituted groups become more aliphatic in character, although no purely aliphatic ketimines have thus far been recorded.

In striking contrast with the generalization of Mignonac, de Booseré reported that his ethyl cyclopropyl ketimine hydrochloride does not appear to be altered either by cold water or even by the action of hot water for several minutes. This observation appeared especially notable in view of a further statement that the compound is decomposed by hot sodium hydroxide solution giving ammonia and an odor analogous to that of ethyl cyclopropyl ketone. The identity of the latter compound appeared to be established conclusively by the formation, but with some difficulty, of its semicarbazone.

In view of the striking resistance to hydrolysis reported for the ethyl cyclopropyl ketimine hydrochloride as opposed to the great sensitivity of its phenyl analog,[5] Professor Julius Stieglitz instituted four years ago a physico-chemical investigation of the ketimines as a class in order to ascertain precisely the relationship existing between their structure, their stability in water and their strength as bases. This line of attack, it was supposed, might connect the striking stability of the ethyl cyclopropyl ketimine hydrochloride with the presence of a large percentage of the enamic tautomer in the equilibrium $—C(=NH)—CH< \rightleftharpoons —C(NH_2)=C<$.[6] Although evidence of this type has been collected for certain ketimines, the investigation by redirecting attention to the preparation of the cyclopropyl ketimines has shown that the stable supposed

---

[4] Mignonac, *Compt.* rend., 170, 936–938 (1920).

[5] Bary, *Bull. soc. chim. belg.*, 31,404 (1922).

[6] The determination of sensitiveness to hydrolysis has been made the basis of a study of ketimine–quinoid–amine tautomerism of phenolic derivatives of benzophenone by J. Stieglitz and J. B. Culbertson (Doctorate "Dissertation," University of Chicago, 1927). Thus the tautomerism $HO—C_6H_3(OH)—C(=NH_2^+)C_6H_5 \rightleftharpoons O=C_6H_3(OH)=C(NH_3^+)—C_6H_5$ reveals itself in the rate of saponification of the ketimine as well as in color and other relations (J. S.).

ethyl cyclopropyl ketimine hydrochloride is in reality the isomeric 2-ethylpyrroline salt, which is perfectly stable in water. In addition the writer has also found that the real cyclopropyl ketimine hydrochlorides also undergo a molecular rearrangement to the pyrroline salts, whereby the unstable triatomic ring is opened and a new stable five-atom ring is closed.

The Formation of 2-Phenylpyrroline from **γ-Chlorobutyronitrile.**—In an attempt to prepare phenyl cyclopropyl ketimine by an extension of the reaction which de Booserk claimed gave ethyl cyclopropyl ketimine, γ-chlorobutyronitrile was treated with magnesium phenyl bromide. The addition product was decomposed by both the acetic acid–ammonia and the ice–ammonium chloride methods as described by Moureu and Mignonac,[7] and also by liquid ammonia as developed by the writer. The evaporation of the dry filtered ether solutions obtained by the foregoing methods on the water-bath gave mainly solid 2-phenylpyrroline hydrochloride accompanied by a variable amount of the free base and other products. It is to be noted that the evaporation and heating on the water-bath led to a chemical change, since the solid hydrochloride is insoluble in ether.

The Origin of the 2-Phenylpyrroline Hydrochloride.—It is clear that the 2-phenylpyrroline hydrochloride resulted from the rearrangement of phenyl y-chloropropyl ketimine. Thus, in the first place, theory would indicate that magnesium phenyl bromide would react normally with γ-chlorobutyronitrile, $Cl—(CH_2)_3—CN$, to give the bromomagnesium derivative of phenyl γ-chloropropyl ketimine, $Cl—(CH_2)_3—C(=NMgBr)C_6H_5$, which by careful decomposition as indicated above would yield the free ketimine, $Cl—(CH_2)_3—C(=NH)C_6H_5$, with certain by-products. It is well known, however, that compounds of the type of the aforementioned ketimine show a general tendency toward internal condensation. Thus, by analogy with the behavior of β-chloro-ethyl imidobenzoate[8] and y-chloropropyl imidobenzoate,[9] it would be expected that phenyl γ-chloropropyl ketimine would rearrange into 2-phenyl-A^1-pyrroline hydrochloride. If, however, the Δ^2 structure, which has been assigned by Gabriel and Colman[10] to the pyrroline hydrochloride finally obtained, is correct, the rearrangement of the ketimine into this compound could be readily understood by assuming the ketimine to be in equilibrium with its enamic tautomer,[11] also called an isoketimine,[12] and that the latter

---

[7] Moureu and Mignonac, *Compt. rend.*, 156, 1801–1806 (1913); *Ann. chim.*, [9] **14,** 322–359 (1920).

[8] Wislicenus and Körber, *Ber.*, 35, 164–168 (1902).

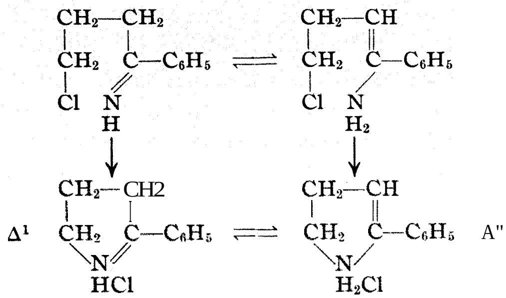
[9] F. A. Keniston, "Thesis," Rensselaer Polytechnic Institute.

[10] Gabriel and Colman, *Ber*, 41, 517–518 (1908).

[11] Compare Thorpe and Best, J. *Chem. Soc.*, 95, 1506 (1909).

[12] Moureu and Mignonac, *Ann chim.*, 14,352 (1920).

then undergoes ring closure. These two possibilities and also a third involving a Δ^1–Δ^2 tautomerism are shown by the following equations[13]



In order to substantiate the foregoing theory, namely, that the action of magnesium phenyl bromide on y-chlorobutyronitrile gives phenyl y-chloropropyl ketimine as an intermediate product, which then rearranges into the phenylpyrroline hydrochloride, an attempt was made to isolate and identify the ketimine.

Phenyl y-Chloropropyl **Ketimine.**—On account of certain concurrent and consecutive reactions associated with the formation of the bromomagnesium derivative of phenyl y-chloropropyl ketimine, and because of the unstable character of the ketimine itself, it was not found possible by the method used to isolate the ketimine in a sufficiently pure state to establish its identity positively by analysis. That this compound was formed, however, is clear from the facts, first, that the bromomagnesium derivative, whose composition closely approximated the theoretical values, gave phenyl y-chloropropyl ketone on hydrolysis, and, second, that the impure ketimine hydrochloride, which was actually separated, gave in one experiment a velocity constant for its reaction with water at 0° whose value, *viz.*, $k, = 0.36 \pm$, was in complete harmony with the estimated order of reactivity, $k_v = 0.371$. The latter value was calculated upon the basis of an extensive comparative study of imido ester and ketimine stability which is being carried out in these Laboratories.

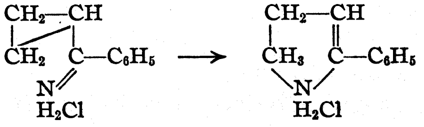
The Origin of the Free **2-Phenylpyrroline.**—The free 2-phenylpyrroline, which is formed in connection with all three decomposition methods, doubtless results from several concurrent and consecutive reactions. In the first place the free base is obtained with ammonium chloride by the action of ammonia on its hydrochloride, which is formed as described above. In the second place the free pyrroline would result from the decomposition of its N-bromomagnesium derivative, which appears to be formed to some extent. In addition a very small portion of the free

---

[13] Since Gabriel presented no critical evidence for the A^2 structure which he adopted, work is being continued on this phase of the problem in conjunction with the synthesis of other pyrrolines and related compounds.

base, which is obtained in connection with the ice–ammonium chloride decomposition method, would be formed by the action of ammonia on the hydrolysis product of the ketimine, namely, the ketone.

The Formation of 2-Phenylpyrroline Hydrochloride from Phenyl Cyclopropyl Ketimine Hydrochloride.—When it was found that phenyl cyclopropyl ketimine apparently could not be obtained directly from γ-chlorobutyronitrile, the original method followed by Bary for the preparation of this compound was employed. In studying the hydrochloride of this ketimine it was found that it melted fairly sharply at about 104–105°, but that it resolidified almost immediately, giving a compound melting from 195–200°. This change was found to be occasioned primarily by the rearrangement of the ketimine hydrochloride into the isomeric pyrroline salt as a result of the rupture of the cyclopropyl ring, as follows



All other cyclopropyl and cyclobutyl ketimine hydrochlorides thus far investigated behave in the same manner.[14]

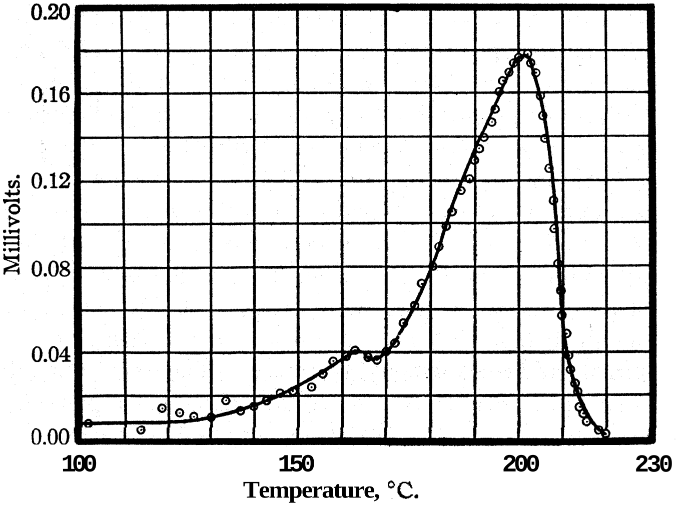


Fig. 1.

The Formation of 2-Phenylpyrroline from Phenyl Cyclopropyl Ketimine.—Although the discovery of the rearrangement of phenyl cyclopropyl ketimine hydrochloride into the isomeric pyrroline salt indicated that the free ketimine base would rearrange similarly, the experimental

---

[14] Baer, Robbins and Van Wyck, "Theses," Rensselaer Polytechnic Institute.

confirmation of this reaction came accidentally as the result of the distillation of a quantity of the free ketimine, which contained some chlorine compound, probably hydrochloride, as an admixture.

In order to avoid future loss of ketimine, comparative measurements were made to ascertain the effect of temperature and the presence of the hydrochloride on the sensitivity of the compound to rearrangement. On account of the scarcity of ketimine and in view of the fact that the ring rupture liberates heat, a differential chromel-constantan thermocouple was employed for the work. One leg of the thermocouple was immersed in the sample and the other in an equal amount of liquid petrolatum. The two tubes were then heated uniformly in a bath and simultaneous minute readings were taken on the thermometer and potentiometer.

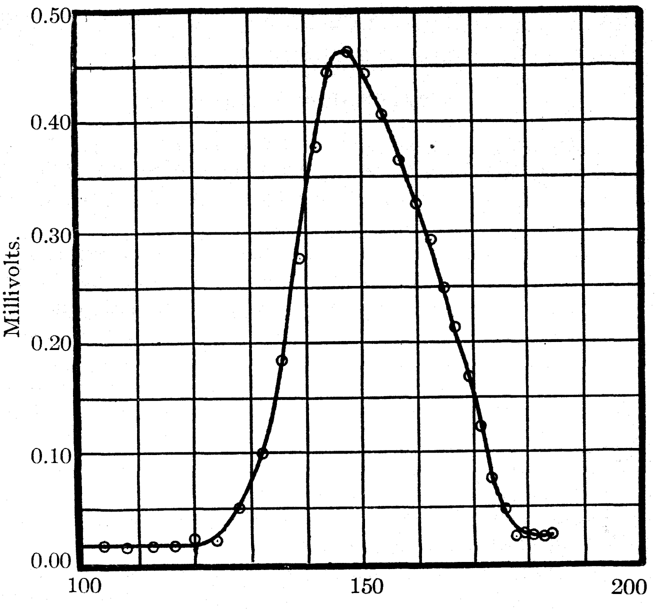


Fig. 2.

Figure 1 represents the effect of heating on the free ketimine, the heating being started at 91°. Exactly the same type of curve was obtained in the case of a second run which was started at 26°. Fig. 2 shows the catalytic effect produced by the addition of **0.0027** g. of the hydrochloride to **0.3483** g. of the free base. The same type of curve was given by the substitution of the same weight of the isomeric pyrroline salt for the ketimine hydrochloride but the maximum reached was somewhat lower, as would be expected. Ketimine free from all traces of hydrochloride would doubtless show a somewhat greater thermal stability than that indicated by Fig. 1.

The greater sensitivity of the phenyl cyclopropyl ketimine hydrochloride to rearrangement as compared with the free base is in complete harmony with the work of several investigators,[15] who have found that the cyclopropyl ring has an increased tendency to rupture in the presence of hydro-halogen acid.

Although practically all of the ketimine is converted into the pyrroline under the conditions mentioned above, other reactions occur. The most obvious of these is the probable formation of ammonia and diphenylcyclopropylcyclopropylidene ketisoketimine, the latter of which would probably undergo ring ruptures analogous to those previously described.

Experimental Part

Preparation of **Nitriles.**—Cyclopropyl cyanide, $\overline{\mathrm{CH_2—CH_2—C}}\mathrm{H—CN}$, was prepared by the action of sodium hydroxide on γ-chlorobutyronitrile, $\mathrm{Cl—CH_2CH_2CH_2—CN}$, which was obtained from trimethylene chlorobromide, $\mathrm{Cl—CH_2CH_2CH_2—Br}$, and potassium cyanide.

The trimethylene chlorobromide was made both by the action of moist hydrogen bromide gas on allyl chloride, $\mathrm{CH_2{=}CH—CH_2Cl}$,[16] according to the procedure described by Bruylants,[17] and also by the refluxing of trimethylene chlorohydrin,[18] $\mathrm{Cl—CH_2CH_2CH_2OH}$, while it was stirred with 48% hydrobromic acid according to the general procedure described by Kamm and Marvel.[19] This latter procedure is much to be preferred. The writer also succeeded in preparing the chlorobromide in one operation from trimethyleneglycol, $\mathrm{HO—CH_2—CH_2—CH_2—OH}$, by several methods, but the yields were comparatively unsatisfactory.

γ-Chlorobutyronitrile was prepared by Henry's method,[20] with the exception that 1.1 mole of potassium cyanide per mole of chlorobromide was found to be slightly more advantageous; moreover, the time of refluxing was increased and the nitrile and alcohol were distilled under diminished pressure.

The cyclopropyl cyanide was obtained by the action of powdered sodium hydroxide on γ-chlorobutyronitrile.[21] The reaction is quite violent and considerable ammonia is given off, the latter resulting from the hydrolysis of the nitriles by the water formed during the reaction. On account of the value of the cyclopropyl cyanide, several methods were studied for minimizing the hydrolysis. The admixture of powdered calcium oxide was of apparent value, but still better results were obtained by the use of anhydrous aluminum oxide, suggested by Dr. F. W. Schwartz. Subsequently it was found that sodamide works quite well. Although still better results may possibly be obtained by employing some of the technique developed by Nicolet and Sattler,[15] for the preparation of this compound, the following typical procedure for the sodium hydroxide–aluminum oxide method is given as a matter of record.

---

[15] Compare Nicolet and Sattler, THIS JOURNAL, **49, 2066–2068 (1927).**

[16] Coffey and Ward, *J. Chem. Soc.*, **119, 1305 (1921).**

[17] Bruylants, *Bull. sci. acad. roy. belg.*, **12, 1085–1094 (1908).**

[18] Hultman, Davis and Clarke, THIS JOURNAL, **43, 369 (1921).**

[19] Kamm and Marvel, *ibid.*, **42, 307 (1920).**

[20] Gabriel, *Ber.*, **23, 1771 (1890).**

[21] Henry, *Bull. sci. acad. roy. belg.*, **[3] 36, 34 (1898).**

A mixture of 40 g. of powdered sodium hydroxide and 15 g. of freshly dehydrated powdered aluminum oxide was introduced into a 250-cc. distilling flask connected with an efficient water condenser. A weight of 75 g. of y-chlorobutyronitrile was then added all at once and the mixture well shaken, giving a uniform paste. The flask and contents were then heated in an oil-bath to about 154°, when a vigorous reaction occurred, necessitating the removal of the oil-bath. When the intensity of the reaction had subsided some hat., the bath wss returned and its temperature gradually raised to about 275°. Finally the receiver and distillate were replaced by a second receiver, when the application of diminished pressure gave a small additional quantity of distillate. The total distillate was washed once with water and then dried. Several similar runs were combined and fractionated with the aid of a special Vigreaux–Hempel column of small diameter and about two feet long, giving results similar to those reported by Bruylants and Stassens,[22] the main fraction boiling from 133–134° at 749 mm.

The Formation of 2-Phenyl Pyrroline, $C_3H_5{-}\overline{C{=}CH{-}CH_2{-}CH_2{-}NH}$, from γ-Chlorobutyronitrile.—Magnesium phenyl bromide was prepared from 8.4 g. of magnesium (2.42 mole), 56 g. of bromobenzene (2.5 mole) and 150 cc. of absolute ether, the procedure employed by Moureu and Mignonac being used.[23] To this ether solution 15 g. (1 mole) of γ-chlorobutyronitrile (b. p. 78–80° at 12 mm.), dissolved in its own volume of ether, was added slowly and with stirring. At the end of about nine minutes crystals separated out, accompanied by vigorous ebullition of the ether. The heating and stirring were then continued for four hours. During this time the material, which was originally crystalline and white, turned dark slowly and took on an amorphous appearance. The mass was then washed with anhydrous ether, when the residue was treated with 24 cc. of glacial acetic acid dissolved in 100 cc. of ether. Stirring and heating on the water-bath were then continued for ten hours, when the mixture was allowed to stand. At this point the yellowish residue was collected on a filter, washed with ether, suspended in more dry ether and then treated with a current of dry ammonia gas for several hours. The ether solution resulting was filtered from the residue (B), and distilled on the water-bath, leaving in the flask a yellowish solid, which was found to be the hydrochloride of a base. Up to this point the writer supposed that he was preparing phenyl cyclopropyl ketimine, but the appearance of the solid showed that some different change had taken place.

Since the residue (B), which was collected on a filter following the action of the ammonia, was found to contain undecomposed organomagnesium derivative, this was decomposed with shaved ice and ammonium chloride; the mixture was then extracted with ether and the ether solution dried over anhydrous sodium sulfate. The dry filtered solution was then evaporated under diminished pressure at a temperature below 0°, leaving a few cc. of a brownish oil. This liquid, contained in a flask, was then heated in a water-bath, when solidification occurred mainly in the vicinity of 85°, although a considerable fraction in this case failed to change.

The two hydrochloride residues thus obtained were dissolved in dry chloroform, the solution treated with dry ammonia gas and, after filtration, the chloroform was distilled off, leaving an oil, which gave about 5 g. of substance boiling between 117–125° at 12 mm. This product was later combined with similar material, which was obtained in the course of a second run not greatly different from the foregoing, and the mixture distilled, giving a liquid boiling for the most part at 124" at 15 mm. (In a subsequent run by a somewhat simplified procedure 8.5 g. of base, b. p. 125–125.5° at 15.5–16 mm., was obtained.) The distillate was colorless at first but it slowly developed a reddish

---

[22] Bruylants and Stassens, Bull. *sci acad.* roy. *belg.*, [5] 7,702–719 (1921).

[23] Moureu and Mignonac, *Ann. chim.*, 14,336 (1920).

tint on standing. It was identified as 2-phenylpyrroline from a study of its hydrochloride.

The hydrochloride was obtained by the action of carefully dried hydrogen chloride gas on a solution of the free base in dry ether. The precipitated hydrochloride was collected on a filter, washed with dry ether and then left overnight in a desiccator containing sodium hydroxide and calcium chloride. The compound was recognized as 2-phenylpyrroline hydrochloride upon the basis of its stability in water, even on boiling, its chlorine content and its conversion into the characteristic picrate and the chloroplatinate of the base. The hydrochloride dissolves readily in chloroform, alcohol and water, but it is practically insoluble in ether and only slightly soluble in carbon tetrachloride.

Anal. Subs., 0.0454: 2.46 cc. 0.1 *N* $AgNO_3$. Calcd. for $C_{10}H_{12}NCl$: Cl, 19.52. Found: 19.24. *Anal.* of chloroplatinate. Subs., 0.0931: Pt, 0.0258. Calcd. for $C_{20}H_{24}N_2Cl_6Pt$: Pt, 27.87. Found: Pt, 27.71.

Isolation of Impure Phenyl **γ-Chloropropyl Ketimine,** $C_6H_5—C(=NH)—CH_2—CH_2—CH_2—Cl$.—An ether solution of magnesium phenyl bromide was prepared from 6.76 g. of magnesium (1.29 mole) and 44.8 g. of bromobenzene (1.33 mole). To this was added 22 g. of γ-chlorobutyronitrile (1 mole) dissolved in its own volume of ether; crystallization occurred as usual. The mixture was then heated for two hours on the water-bath and allowed to stand for twelve hours. At this time the precipitate was brought onto a filter, washed three times with anhydrous ether, decomposed with shaved ice and ammonium chloride, extracted four times with ether and the ether solution finally dried over anhydrous sodium sulfate. Two portions of this solution were next removed with the hope of being able to separate the free ketimine from the first portion and its hydrochloride from the second.

Free Base.—The ether was removed from portion No. 1 by evaporation under diminished pressure at less than room temperature. Since solid began separating as the result of a reaction almost as soon as the ether was removed, samples of the brownish liquid were taken immediately.

Anal. Calcd. for $C_{10}H_{12}NCl$: N, 7.71; Cl, 19.52. Found: 5.73; 16.12.

The amount of acid neutralized by the residue also was only in qualitative accord with the ketimine theory.

Hydrochloride.—A current of dry air was aspirated through the second ether portion in order to remove any ammonia. Pure dry hydrogen chloride gas was next passed into the cold ether solution, giving a yellow viscous mass which adhered to the flask tenaciously. The ether was poured off, the residue dissolved in dry chloroform and reprecipitated with dry ether, giving the same kind of viscous product as before. However, by repeating this procedure several times a product was finally obtained which solidified when rubbed with a glass rod. This solid hydrochloride, which was brought on a filter in dry air, was impure, as was shown by its melting incompletely in the vicinity of 85–88°, and also by its analysis.

Anal.[24] Calcd. for $C_{10}H_{13}NCl_2$: N, 6.42; Cl, 32.52. Found: N, 8.10; Cl, 32.40.

The most significant property of this hydrochloride was its remarkable rate of reaction with water at 0°. The procedure followed for the measurements was the same in principle as that developed by Stieglitz and Derby for the imido-ester hydrochlorides.[25] In the following table Col. 2 gives

---

[24] The writer is indebted to Mr. F. A. Keniston for these Cl and N determinations.

[25] Derby, *Am.* Chem. J., 39, 439441 (1908).

the cc. of $N/10$ sodium hydroxide neutralized by the ketimine hydrochloride in *10* cc. of solution, containing *10.9* g. per liter, at the end of times t_1, t_2..... The constant k is calculated from the expression for a monomolecular reaction

$$k = \frac{2.303}{t_2 - t_1} \log \frac{v_1}{v_2}$$

where v_1, v_2 represent the cc. of $N/10$ sodium hydroxide in Col. 2, and the correction of t_1, t_2 from seconds to minutes is made.

TABLE I

DECOMPOSITION OF PHENYL γ-CHLOROPROPYL KETIMINE HYDROCHLORIDE

Time from start, sec.	30	76	145	180	
Vol. of $N/10$ NaOH, cc.	3.35	2.50	1.96	1.16	
k	..	0.386	0.280	0.425	Av. 0.363

Relatively large experimental errors were unavoidable on account of the exceedingly high reaction rate of the compound.

Analysis of Bromomagnesium Derivative of the **γ-Chloropropyl** Phenyl **Ketimine,** $(ClCH_2CH_2CH_2)(C_6H_5)C{=}NMgBr$.—Magnesium phenyl bromide was added to y-chlorobutyronitrile as previously described, but without any subsequent heating. A portion of the carefully washed crystalline mass was analyzed after several hours' exposure in a vacuum desiccator at 50°.

Anal. Subs., 0.1233: MgO, 0.0178. Subs., 0.03132: cc. of $N/100$ HCl, 9.85. Calcd. for $C_{10}H_{11}NClBrMg$: Mg, 8.54; N, 4.91. Found: Mg, 8.71; N, 4.40.

Previous analytical results indicate that the compound crystallizes with a molecule of ether.

Phenyl **γ-Chloropropyl** Ketone, $C_6H_5—CO—CH_2CH_2CH_2Cl$.—The above magnesium compound was decomposed with aqueous hydrochloric acid and the mixture extracted with ether. The ether solution was dried over calcium chloride and then treated with dry hydrogen chloride gas in order to precipitate any 2-phenylpyrroline as hydrochloride, some of this being obtained. After standing for a day the ether was removed from the filtered solution, leaving an oily residue. This was fractionated several times through a short column, giving a nitrogen-free oil which boiled mainly from 130–133° at 4 mm.

Anal. Subs., 0.1689: AgCl, 0.1256. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 18.40.

Several further rectifications gave a liquid of boiling point 120–121° at 3 mm.; d_4^{20}, 1.149; n_D^{20}, 1.55433.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 16.79.

The lower chlorine content was probably occasioned by the loss of hydrogen chloride accompanied by the formation of phenyl cyclopropyl ketone.

Semicarbazone of Phenyl **γ-Chloropropyl** Ketone.—The semicarbazone separated out after a day in the form of colorless crystals melting at 136–137°. Prolonged heating leads to some decomposition, possibly to carbamyl-1-phenyl-3-tetrahydropyridazine.[26] The semicarbazone was analyzed according to Pregl's micro methods.

Anal. Subs., 9.98 mg.: N_2, 1.500 cc. (as measured at 16°, 765.9 mm.). Subs., 14.70 mg.: AgCl, 8.90 mg. Calcd. for $C_{11}H_{14}ON_3Cl$: N, 17.53; Cl, 14.80. Found: N, 17.54; Cl, 14.98.

---

[26] Compare Wohlgemuth, *Ann. chim.*, [9] 2, 454 (1914).

The Formation of 2-Phenylpyrroline from Phenyl γ-**Chloropropyl** Ketone.—Hielscher's preparation of 2-methylpyrroline by the action of ammonia on methyl γ-bromopropyl ketone[27] led Wohlgemuth[28] to attempt the extension of the reaction. He found, however, that the interaction of ammonia and γ-chloro-*n*-butyl ethyl ketone gave methyl cyclopropyl ethyl ketone, that is, methyl-1-propionyl-2-cyclopropane. He was unable to identify any pyrroline. The writer, on the other hand, has been partially successful in a similar case, as described below.

Phenyl y-chloropropyl ketone was treated with an excess of cold alcoholic ammonia for three weeks. The solution was dried over anhydrous sodium sulfate, filtered and the alcohol completely removed by evaporation at ordinary temperatures under diminished pressure after the addition of a little ether. The residue was dissolved in dry ether, treated with a slight excess of dry hydrogen chloride and allowed to stand until the 2-phenyl pyrroline hydrochloride had completely precipitated. The solid, obtained in about 10% yield, was identified as 2-phenylpyrroline hydrochloride upon the basis of its melting point and the formation of the picrate. The ether was removed from the remaining solution leaving an oily residue, apparently composed of the unchanged original ketone mixed with phenyl cyclopropyl ketone.

Since bases, in general, tend to form cyclopropyl derivatives from y-chloropropyl compounds, it follows that any free pyrroline base, for example 2-phenylpyrroline, must not be distilled in the presence of a y-chloropropyl ketone such as the y-chloropropyl phenyl ketone, which is a by-product of one method previously described for the preparation of pyrrolines. The heating results in the formation of the pyrroline hydrochloride which condenses in the flask neck.

The Formation of 2-Phenylpyrroline from Phenyl **Cyclopropyl Ketimine,** $C_6H_5—C(=NH)—\underline{CH—CH_2—CH_2}$.—Although the original object in the preparation of the phenyl cyclopropyl ketimine was to obtain the pure free base and its hydrochloride for certain physico-chemical measurements, lack of precise knowledge regarding the stability of the ketimine at that time led to the accidental synthesis of the isomeric pyrroline.

Phenylmagnesium bromide was prepared from 14.6 g. of magnesium (1.46 mole), 94.2 g. of bromobenzene (1.5 mole) and 250 cc. of anhydrous ether. To this solution 26.8 g. (1.0 mole) of cyclopropyl cyanide (b. p. 133–134° at 749 mm.), dissolved in its own volume of ether, was added over an interval of four minutes. After remaining quiescent for six minutes a light grey or slate-colored precipitate separated from the solution, occasioning such vigorous boiling of the ether that prompt cooling in water was necessary in order to prevent the expulsion of the mixture through the condenser. The ketimine was next liberated from the well-washed bromomagnesium derivative by the action of shaved ice and ammonium chloride; it was immediately separated by several extractions with ether, the extract being dried at once with calcium chloride followed by anhydrous sodium sulfate. By treating this solution with dry hydrogen chloride the ketimine was precipitated in the form of its hydrochloride, which was then dissolved in hot, dry chloroform and reprecipitated by ether as beautiful white crystals containing a molecule of chloroform. With the expectation of obtaining the pure free base and its hydrochloride for the physico-chemical measurements, the crystals containing the added chloroform were dissolved in warm chloroform; the solution was treated with an excess of dry ammonia gas, following which the precipitated ammonium chloride was removed by filtration and the chloroform by distillation on the water-bath. Since the free ketimine thus obtained was slightly colored, it was erro-

---

[27] Hielscher, *Ber.*, 31,277 (1898).

[28] Wohlgemuth, Ann. *chim.*, [9] 2,441 (1914).

neously decided to risk the distillation process in order to obtain a colorless product, but during the attendant heating under diminished pressure the ketimine rearranged into the isomeric pyrroline, as was conclusively demonstrated by the study of the hydrochloride described below. The rearrangement appeared to be accompanied by a peculiar color change associated with more vigorous boiling. About 90% of the ketimine was obtained as the pyrroline; the brownish-red residue was not examined.

In passing it may be noted that, although an excess of dry ammonia gas was employed in the foregoing procedure, a number of crystals of the hydrochloride of some base collected in the neck of the Claisen flask at the end of the distillation. These together with the excessive temperature, as was learned later, were responsible for the sensitivity of the ketimine to rearrangement. The crystals softened at 67° and melted from 71–73". The nature of this compound, of which only a few milligrams was obtained, may be cleared up in connection with work on other pyrrolines.

2-Phenylpyrroline Hydrochloride.—The distilled 2-plienylpyrroline, obtained as described above, was dissolved in dry ether, treated with dry hydrogen chloride and the salt removed by filtration.

Anal. Subs., 12.08 mg.: cc. $N/100$ HCl, 6.62. Subs., 0.4366: cc. $N/10$ $AgNO_3$, 23.96. Calcd. for $C_{10}H_{12}NCl$: N, 7.71; Cl, 19.52. Found: N, 7 67; Cl, 19.46. ***Anal.*** of chloroplatinate. Subs., 8.00 mg.: Pt, 2.23 mg. Calcd. for $C_{20}H_{24}N_2Cl_6Pt$: Pt, 27.87. Found: Pt, 27.87.

Phenyl Cyclopropyl Ketimine.—The ketimine which was employed in securing data for Figs. 1 and 2 was obtained by the evaporation of the ether at less than room temperature from a filtered dry ether solution obtained as described in the preceding section on the formation of 2-phenylpyrroline from phenylcyclopropyl ketimine with the single exception that the Grignard reagent was prepared in an atmosphere of dry hydrogen.

The Formation of 2-Ethylpyrroline Hydrochloride from γ-Chlorobutyronitrile.—By the action of magnesium ethyl bromide on y-chlorobutyronitrile, de Booseré, as stated previously, obtained the hydrochloride of a base, identified by him as ethyl cyclopropyl ketimine. This compound, which distilled from 160–170° (14–16 mm.), was very deliquescent and was apparently unattacked by water. When treated with sodium hydroxide solution, however, it was stated to decompose into ammonia arid ethyl cyclopropyl ketone, the presence of the latter being inferred upon the basis of odor and the formation of the semicarbazone. The free base, which was obtained from the hydrochloride, boiled from 127–128° at 759 mm. Although it appeared clear that the base was actually 2-ethylpyrroline,[29] in spite of the behavior with semicarbazide, the reaction has been reinvestigated.

Magnesium ethyl bromide was prepared from 8.4 g. of magnesium, 39 g. of ethyl bromide and 145 cc. of ether. To this solution 15 g. of y-chlorobutyronitrile dissolved in its own weight of ether was added, no permanent separation of solid occurring. The solution was then allowed to simmer gently for half a day, at which time the greenish-yellow liquid was poured into water containing ammonium chloride and the solution extracted with ether. Since distillation of the dried ether extract failed to give a constant-boiling fraction, the combined non-ethereal fractions were treated with alcoholic ammonia for a day, at which time the alcoholic solution was neutralized with anhydrous hydrogen chloride. The ammonium chloride was removed by filtration and the filtrate distilled, giving a substance which passed over mainly at 166° (18 mm.) and which solidified on cooling. The compound was so deliquescent that no accurate melting point could be determined by the capillary tube method, values being obtained ranging from 87–101°, these being surprisingly close to the melting point of the real ethyl cyclo-

---

[29] Dennstedt, German Patent 127,086; *Chem. Zentr.*, [1] 338 (1902).

propyl ketimine hydrochloride. Recrystallization from acetic anhydride and dry ether gave nice crystals but these deliquesced immediately when exposed to the outside air. The compound, like that of de Booseré, was not apparently altered either by hot or cold water. When treated with sodium hydroxide, an odor was at once developed which, indeed, resembled that of a mixture of ammonia and ethyl cyclopropyl ketone, as previously reported. That this was an olfactory error was shown by the fact that an alcoholic solution of the hydrochloride gave a precipitate with alcoholic platinic chloride, which, after resolution in boiling alcohol and reprecipitation by anhydrous ether, was found to be the chloroplatinate of 2-ethylpyrroline, m. p. 179–180° with decomposition.

Anal. of chloroplatinate. Subs., 9.33 mg.: Pt, 3.00 mg. Calcd. for $C_{12}H_{24}N_2Cl_6Pt$: Pt, 32.35. Found: Pt, 32.15.

Dennstedt, who first prepared the chloroplatinate in an impure form, found that it melted in the vicinity of 170°.

That the hydrochloride is not hydrolyzed to ammonia and ketone when distilled with a base was shown by the separation of the same chloroplatinate from an aqueous distillate, which was obtained by distilling the hydrochloride with aqueous sodium hydroxide.

The Formation of 2-Ethylpyrroline Hydrochloride from Ethyl Cyclopropyl Ketimine Hydrochloride.—Ethyl cyclopropyl ketimine was prepared from magnesium ethyl bromide and cyclopropyl cyanide by the acetic acid–ammonia process of Moureu and Mignonac. During the work certain unexpected difficulties arose which necessitated the exposure of the mixture to the outside air for a short time. Since this led to some hydrolysis of the very sensitive ketimine, the pure compound will be described later. Semi-quantitative work relating to its stability, however, shows that it is very rapidly hydrolyzed by water to give the ketone and ammonia. A portion of the ketimine was heated in a sealed tube up to 185° in order to learn how sensitive it is to rearrangement. No pyrroline, however, was separated.

A small amount of the impure ketimine was converted into its hydrochloride. This melted between 101–103°, decomposing shortly afterward. From a portion heated to 130° the chloroplatinate of the 2-ethylpyrroline was obtained.

Anal. of chloroplatinate. Subs., 7.33 mg.: Pt, 2.36 mg. Calcd. for $C_{12}H_{24}N_2Cl_6Pt$: Pt, 32.35. Found: Pt, 32.19.

In passing it may be added that the real ethyl cyclopropyl ketimine hydrochloride is decomposed normally by water, although it is more stable than was expected. This is being investigated further.

The writer is indebted to Professor Julius Stieglitz, under whose direction the work was undertaken, for criticism, inspiration and advice, and to President P. C. Ricketts and Professor A. W. Davison for their aid in providing materials and equipment.

Summary

1. 2-Phenylpyrroline can be obtained as a result of the action of magnesium phenyl bromide on γ-chlorobutyronitrile. By the procedure described most of the pyrroline is initially obtained in the form of its hydrochloride, which results from the rearrangement of phenyl γ-chloropropyl ketimine.

2. By heating phenyl cyclopropyl ketimine hydrochloride above its melting point it rearranges into 2-phenylpyrroline hydrochloride.

3. 2-Phenylpyrroline is formed by the action of heat on phenyl cyclopropyl ketimine. Curves are given which show the effect of temperature and the presence of the ketimine hydrochloride on the stability of the ketimine base.

4. The facts enumerated in 1, 2 and 3, together with a general study of ketimine stability, have led to the proof that de Booseré's so-called ethyl cyclopropyl ketimine hydrochloride, which is described as remarkably stable toward hydrolysis, is in reality a pyrroline derivative. The true ethyl cyclopropyl ketimine hydrochloride is sensitive to hydrolysis, as are the other true ketimine hydrochlorides.

CHICAGO, ILLINOIS

[CONTRIBUTION PROM THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

PROCESSES INVOLVED IN THE DECOMPOSITION OF WOOD WITH REFERENCE TO THE CHEMICAL COMPOSITION OF FOSSILIZED WOOD[1]

BY SELMAN A. WAKSMAN AND KENNETH R. STEVENS

RECEIVED OCTOBER 1, 1928 PUBLISHED APRIL 5, 1929

Our information concerning the chemical processes involved in the decomposition (or so-called "decay") of wood, fossilization being merely a type of decomposition, is very meager. The question as to whether decomposition, which is never complete and which results only in a partial reduction in the bulk of woody substance, consists in the gradual utilization by microorganisms (fungi and bacteria) of all the chemical constituents of wood or whether certain complexes are decomposed more readily than others, has aroused considerable discussion. The nature of the processes involved in the decomposition of wood and other plant substances has found special application in connection with the recently proposed theories of the origin of coal and peat, largely centering upon the role of celluloses and lignins in this process.

It is commonly assumed that the disintegration of wood consists, first, in the chemical simplification of the various constituents from *a* greater to a lesser complexity, finally leading to their transformation into carbon dioxide, ammonia, water and, under anaerobic conditions, also into hydrogen and methane. The assumption that a number of intermediary substances are formed in this process has never been sufficiently substantiated.

Investigations reported elsewhere[2] on the decomposition of plant residues by microorganisms brought out the fact that the water-soluble plant constituents are the first to be attacked, long before the hemicelluloses

---

[1] Journal series paper of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

[2] S. A. Waksman and F. G. Tenney, *Soil Science*, 24, 275–284 (1927); 26, 155–171 (1928).

and celluloses are acted upon. No intermediary products at all or only in mere traces were found in the decomposition of celluloses by pure cultures of fungi[3] under controlled laboratory conditions; practically all of the carbon of the celluloses decomposed by these organisms was accounted for either in carbon dioxide given off or in the cell substance synthesized by the organisms. In view of the fact that this microbial cell substance frequently contains a large amount of cold and hot water-soluble material, the increase observed by Bray and Andrews in the water-soluble constituents as a result of decomposition of wood by fungi may be due to this cause rather than to the formation of intermediary products. The reasons submitted by Hawley and Wise[4] why these results must be considered in the light of the formation of intermediary compounds in the destruction of lignins and celluloses in wood are not very convincing. If one only recalls that large quantities of fungus mycelium are synthesized in the process of decomposition of the wood and that this mycelium is rich not only in water-soluble substances but also in various hemicellulose-like or gum-like substances, we can account even for the increase in the alkali-soluble materials as a result of wood decomposition.

In connection with a study[5] of the formation of "humus"-like substances from pure celluloses by microorganisms, it has been shown that the organic matter resulting from the repeated decomposition of celluloses, under controlled laboratory conditions and in pure sand but in the presence of additional inorganic nitrogen compounds and other minerals necessary for the growth of the microorganisms decomposing the celluloses, was a product which contained 23.4–30.2% of cold water-soluble, 6.9–13.4% of hot water-soluble and 23.8–25.4% of alkali-soluble (after cold and hot water treatment) material, all of which was a part of the cells of living and dead microorganisms.

There is no doubt that when celluloses are decomposed by anaerobic bacteria large quantities of organic acids and alcohols are produced, but these should be considered as final products of anaerobic metabolism rather than as intermediary products; these acids and alcohols will be decomposed further when conditions are made aerobic and the reaction is favorable.

We have no justification as yet for speaking therefore of the "simplification" of complex plant constituents when these plants are decomposed by fungi. There is more sound evidence that the chemical processes involved in the decomposition of wood by microorganisms consist merely in the complete destruction of the more readily available substances, followed

---

[3] H. Heukelekian and S. A. Waksman, J. *Biol. Chem.*, 66, 323–342 (1925).

[4] L. F. Hawley and L. F. Wise, "The Chemistry of Wood," The Chemical Catalog Company, Inc., New York, 1926, p. 301.

[5] S. A. Waksman, *Cellulosechemie*, 8, H. 9/10 (1927).

by a slow but gradual disappearance of those that are less readily decomposed; the more resistant plant constituents contribute to the formation of the residual (or fossilized) material.

Chemists are willing to agree that the disintegration of wood is largely a result of the activities of bacteria and fungi and that the nature of decomposition depends upon the nature of the organisms that bring about the process. Unfortunately, the chemistry of wood, as well as of natural organic materials in general, still represents a series of complicated problems, and, unless these are first carefully worked out, one could not expect to unravel the chemistry of decomposed wood, as well as of the residual soil humus and peat, and understand the nature of the chemical and biological processes involved in their formation from the natural materials.

It is sufficient to call attention to the chemical composition of the lignins and celluloses in wood, which make up, in the form of lignocelluloses, 65 to 70% of the constituents of the wood. The chemical nature of these substances obtained from wood is influenced quite markedly by the method used in their preparation. When one attempts to determine lignin quantitatively, he is faced with an array of methods which give varying results not only quantitatively but even qualitatively, yielding substances which vary considerably in their chemical nature and their biological behavior. The quantitative determination of cellulose is also apt to give varying results, depending on the method employed, especially if one does not use sufficient care in accounting for the admixture of hemicelluloses, lignins and cutins. It is not remarkable therefore that the results obtained on the decomposition of plant materials are very conflicting, and it is only within very recent years that definite light has been thrown upon the chemical nature of the processes involved.

Rose and Lisse[6] have shown that when wood is rotted by fungi there is a gradual decrease in the cellulose and pentosan content and an increase in the lignin, *as* determined by the methoxyl content, and the amount of alkali-soluble materials. Lignin, which is more resistant to decomposition by microorganisms, gradually accumulates, while the celluloses and hemicelluloses disappear.

These results were utilized by Fr. Fischer[7] to prove his theory that coal originates from the lignins of plant materials, since they resist decomposition, while the other plant constituents, namely, the celluloses, hemicelluloses, proteins, etc., are gradually broken down by microörganisms.

Lamarlière[8] has shown previously that coniferous wood freshly removed from peat beds preserves, the microscopic structure, but a chemical analysis

[6] R. E. Rose and W. M. Lisse, *J. Ind. Eng. Chem.*, 9, 284–287 (1917).

[7] Fr. Fischer and H. Schrader, *Brennstoff-Chem.*, **2**, 37–45 (1921).

[8] L. G. de Lamarlière, *Compt. rend. acad. sci.*, 131, 511–512 (1900).

shows that the celluloses are largely gone, while the amorphous residue dissolves rapidly, after treatment with chlorine, in alkalies.

The nature and rapidity of decomposition of wood depend upon the nature of the infecting organism. Bray and Andrews[9] found that certain hymenomycetes causing brown rot of wood may bring about a loss of **10** to 50% of the wood in six to ten months. The cellulose may be reduced from **60** to 6% in one year, while the loss in the lignins was only **3%;** this small loss all can be accounted for by a loss in the methoxyl content (2.8%).

However, although the lignins are not decomposed as rapidly as the celluloses, hemicelluloses and proteins, they will still undergo some decomposition, slow to be sure, under aerobic conditions. The existence of organisms capable of attacking lignins has now been definitely established.[10]

As a matter of fact, it has been demonstrated[10a] that decomposition of wood, under aerobic conditions and largely through the agency of fungi, can either consist in a rapid disintegration of the celluloses with the accumulation of lignins or in a gradual decomposition of both the celluloses and the lignins and frequently even in an accumulation of cellulose. These two processes were termed by Falck as "destruction" and "corrosion." They account for the differences observed in the chemical composition of the wood decomposed by the brown and white rot-producing fungi.

When a comparison is made of sound and decomposed wood, using the same method of chemical analysis, we can readily recognize the chemical changes that have taken place as a result of the decomposition of the various constituents of the wood by different groups of microörganisms. A typical analysis is given in Table I, where the chemical composition of healthy chestnut and cypress wood is compared with the composition of two samples of decomposed wood, one of which was non-fibrous in nature, having undergone the so-called process of "destruction," and the other fibrous in nature, having been decomposed by the fungi bringing about "corrosion," according to Falck's nomenclature. These results show that while in the case of certain processes of wood decomposition the celluloses have practically all disappeared (even more so than the hemicelluloses) and most of the decomposed wood consists of lignin which has resisted decomposition, in other cases both the lignins and celluloses, as well as the hemicelluloses, have all undergone a gradual decomposition. It is unfortunate that in this particular experiment the samples of decomposed wood were selected at random from decomposing trees in a New England forest and were not studied under controlled laboratory conditions. However, in other investigations on the decomposition of plant materials[11]

---

[9] M. W. Bray and T. M. Andrews, *Ind. Eng. Chem.*, 16, 137–139 (1924).

[10] (a) R. Falck, *Ber.*, 60, 226–232 (1920); (b) S. A. Waksman, F. G. Tenney and K. R. Stevens, *Ecology*, 9, 126–144 (1928).

[11] Results to be published soon in *Soil Science.*

TABLE I

CHEMICAL COMPOSITION OF DECOMPOSED WOOD AS COMPARED WITH HEALTHY WOOD
On percentage basis of dry material

Chemical complexes	Sound wood Chestnut	 Cypress	Rotted wood Non fibrous decomposed wood[a]	 Fibrous decomposed wood[b]
Ether-soluble	2.66	3.53	1 48	6.31
Cold and hot water-soluble	7.08	3.18	1.26	5 61
Alcohol-soluble	3.27	1.92	5.05	3.30
Hemicelluloses	15.23	11.16	4.72	14.43
Celluloses	32.58	37.62	2.16	27.78
Lignins[c]	22.05	28.21	7114	2361
Protein	0.54	0.66	1.31	2.18
Ash	.54	.76	0.65	2.25
Total accounted for	83.95	87.04	87.77	8607

[a] Wood which has undergone the so-called process of "destruction."

[b] Wood which has undergone the so-called process of "corrosion."

[c] Free from ash and nitrogen.

which were carried out under controlled laboratory conditions, it has been found that under anaerobic conditions lignins do not decompose at all or only in mere traces due to the absence of specific organisms, while, under aerobic conditions, the lignins are slowly decomposed, but here as well they are found to be the most resistant group of plant constituents.

It is interesting to observe in Table I the increase in the protein content of the decomposed wood over the sound wood; this is not necessarily due to the accumulation of the proteins because they are more resistant to decomposition by microorganisms than the celluloses, but to the fact that the products of protein decomposition are immediately reassimilated by the microorganisms bringing about the decomposition and are thus preserved. This has been amply demonstrated in this Laboratory for the decomposition of various plant substances by pure and mixed cultures of microorganisms under controlled conditions.

The chemical nature of the transformation of the wood constituents, especially the celluloses and lignins, has attracted considerable attention. According to Wehmer,[12] the wood-destroying fungus *Merulius* lacrymans brings about the decomposition of the cellulose and the transformation of the lignin of the wood into "humin," a part of which is soluble in alkalies and precipitated by acids.

According to Kürschner,[13] various wood-destroying fungi, such as *Merulius* lacrymans, attack largely the cellulose in the wood, while the lignins are transformed into a complex mixture of changed and unchanged depolymerized substances of a humic-like nature. Strache[14] analyzed the inner portion of a 1000-year old pine and found that only traces of cellulose

---

[12] C. Wehmer, *Ber.*, 48, 130–134 (1915); *Brennstoff-Chem.*, 6, 101–106 (1925).

[13] K. Kürschner, Z. *angew. Chem.*, 40, 224–232 (1927).

[14] H. Strache, *Brennstoff-Chem.*, 9, 21–22 (1927).

were left, while the lignin had changed, in the absence of oxygen, into "humic acid," which was thus considered to be the first step in the formation of lignite and brown coal. The residue of the action of *Merulius lacrymans* upon pine wood was found by Schwalbe and Ekenstam[15] to consist of 73% of lignin, 15% of cellulose, 8% of other carbohydrates and 4% of resins; the fats and pentosans were all destroyed; 64.2% of the lignin was soluble in 5% sodium hydroxide solution and it had less methoxyl (10.2%) than lignin of fresh wood. Brandl[16] recorded the presence of 24.90% of acid-hydrolyzable material, including 8.1% of cellulose, and 75.1% of non-hydrolyzable material in decomposed oak wood; the latter fraction was separated into lignin (36.35%) and humic acid (38.75%) on the basis of solubility in sodium bicarbonate solution.

Marcusson,[17] in an attempt to prove by chemical theories and facts the idea of the older botanists and geologists that coal originates largely from celluloses, claims that as a result of decomposition of plant materials the celluloses are changed to oxycelluloses by the action of air, light and moisture; the oxycelluloses are then transformed into "humic acids," which are soluble in dilute alkalies. The role of microorganisms in the processes of decomposition is not considered at all. According to Marcusson, the results of Rose and Lisse[6] could not be used in proving Fischer's theory concerning the role of lignins in coal formation, since the former did not determine the actual lignin content of the various forms of wood, but merely measured the methoxyl content and the amount of alkali-soluble material. Since the methoxyl content of various lignin preparations varies and since it is also present in other substances, as pectins, it need not be taken as an index of the lignin content of wood at various stages of decomposition. Marcusson found that when healthy and rotten wood were treated first with a 1% solution of sodium hydroxide and the lignin determined on the insoluble residue by the Willstatter method, the cellulose was found to decrease from 58% in healthy wood to about 6.0% in the fully rotted wood, while the lignin content was practically the same, ranging from 20 to 23%. The results of Rose and Lisse are explained by Marcusson by the fact that pectins present in the middle lamella and certain waxes also contain methoxyl groups, while the increase in the alkali-soluble materials is explained by the assumption that glucuronic acid, a constituent of oxycellulose, is thereby made soluble.

Without going into a detailed review of the extensive literature on the origin and chemistry of soil "humus," peat and coal, which is found elsewhere,[18] the results of some experiments will be presented here to show that

---

[15] C. G. Schwalbe and A. Ekenstam, *Cellulosechemie,* 8, 13–15 (1927).

[16] A. Brandl, *Brennstoff-Chem.,* 9, 89–94 (1928).

[17] J. Marcusson, *Z. angew. Chem.,* 39, 898–900 (1926); **40,** 48, 1105 (1927).

[18] S. A. Waksman, *Soil Science,* 22, 123–162 (1926).

Marcusson's explanations will not stand any broad generalization and are merely isolated instances which have no application at all to the formation of "humus," peat and coal. The methods of analysis of the various plant constituents are reported in detail elsewhere.[19]

Table II gives an analysis of two samples of wood obtained from an undrained lowmoor peat bog, at Newton, N. J., at a depth of 7–8 feet, and of fossilized wood of the Pleistocene period kindly supplied to the authors by Dr. David White of the U. S. Geological Survey. The composition of these can be compared with that of healthy wood reported in Table I.

TABLE II

CHEMICAL COMPOSITION OF TWO SAMPLES OF FOSSILIZED WOOD

Percentage of dry material

Material	Wood from peat	Fossilized wood (oak)
Ether-soluble material	1.54	0.84
Cold and hot water-soluble organic matter	0.87	0.56
Alcohol-soluble	1.34	1.82
Hemicelluloses	8.15	3.79
Celluloses	6.12	3.38
Lignins (free from nitrogen and ash)	65.02	70.74
Protein	5.37	2.21
Ash	3.85	4.40
Total accounted for	92.25	87.74

The results show that in the wood from peat and in the fossilized wood there is a considerable reduction to an almost complete disappearance of the water-soluble substances; there is also a reduction in the ether-soluble substances and hemicelluloses and a marked decrease in the celluloses. The lignin and ash content have increased to such an extent that they account for three-quarters of the total wood material or of 80% of the constituents accounted for. The proteins also have increased very markedly, from about 0.6% in healthy wood to 2.21% in the fossilized wood and 5.37% in the wood from the lower layers of the peat bog. These results are in full accord with those obtained in this Laboratory experimentally, under controlled conditions, on the decomposition of natural plant materials by microorganisms, which can be summarized by a rapid reduction in the water-soluble substances, decomposition of hemicelluloses and celluloses as well as of certain ether-soluble substances, and an increase in the lignin, ash and protein content. The changes in the nature and quantity of the latter are especially illuminating, since they depend not only on the nitrogenous constituents but also on the nature and amount of the celluloses and hemicelluloses in the plant material, organisms active in the decomposition processes and the conditions under which decomposition is carried out.

[19] S. A. Waksman and K. R. Stevens, *Soil Science,* 26,113–138 (1928).

To demonstrate whether Marcusson is justified in assuming that, after treatment of rotted wood with an alkali solution to remove the so-called "oxycelluloses," the same percentage of lignin will be found in the decomposed as in the healthy wood, the wood from peat and the fossilized wood were subjected to treatment with ether for fifteen hours in Soxhlets, followed by 95% alcohol for one hour at boiling temperature, then boiling for five hours with a 2% hydrochloric acid solution. The lignin content was determined (by adding to a weighed quantity of dry residual material 10 volumes of 80% sulfuric acid, allowing to stand in the cold for two hours, then diluting with fifteen volumes of water and heating at 120° for one hour)[20] in the wood thus treated as well as in the original material and in the wood treated with a 2% sodium hydroxide solution for one hour on a water-bath. The lignin was filtered off, dried and weighed. The ash and nitrogen content of the lignin residue were determined and subtracted to give the amount of lignin.

The results presented in Table III show that the lignin content of untreated wood is somewhat higher than that of wood which has been previously extracted with ether, alcohol and dilute acid. The lignin content of the wood extracted with a 2% sodium hydroxide solution is considerably lower than the lignin of the wood not so treated; however, when the alkaline extract is neutralized with hydrochloric acid and the precipitate formed thereby dried and weighed, it is found that the sum of the weight of the precipitate and the weight of the lignin in the alkali-treated wood is almost the same as the weight of the lignin in the untreated wood. In other words, the alkali treatment merely removed a part of the lignin, or a modified form of lignin, as a result of the activities of microorganisms. Hawley and Campbell[21] found that when Sitka spruce is extracted with 1% sodium hydroxide solution on a boiling water-bath for one hour, the lignin content decreased from 29.3 to 27.7%. Others found that with the advance of decomposition there is an increase in the amount of lignin soluble in alkali bicarbonate or cold alkali hydroxide solutions (so-called "humic acids"). The accumulation of lignin as a result of disintegration of wood under anaerobic conditions is due entirely to its resistance to decomposition under these conditions and not to its formation in the process of decomposition.

TABLE III

LIGNIN CONTENT OF FOSSILIZED WOOD, SUBJECTED TO DIFFERENT PRELIMINARY TREATMENTS (PERCENTAGE OF TOTAL ORIGINAL DRY MATERIAL)

Material	Wood from peat bog	Fossilized wood
Untreated	72.76	84.58
Treated with ether, EtOH and 2% HCl	65.02	70.74
With 2% NaOH for 1 hour at 100°	54.52	56.61
Ppt. of alkaline extract with HCl	10.94	20.38

---

[20] It may be stated here that the lignin obtained by this method compares very well quantitatively with the amount of lignin found by the original hydrochloric acid method of Willstätter or any of its modifications.

[21] L. F. Hawley and W. G. Campbell, *Ind. Eng. Chem.*, 19, 742–744 (1927).

To study the effect of alkali treatment upon the acid lignin obtained from natural and from decomposed plant material, several plant-lignin and peat-lignin preparations were subjected to treatment with 2% sodium hydroxide solution, either in the cold for twenty-four hours, or for one hour on a steam-bath, or for thirty minutes at 120° (1-g. portions of lignin were extracted with 100 cc. of the sodium hydroxide solution). The solutions were then filtered and the residues washed, dried and weighed; hydrochloric acid was then added to the solutions and the precipitates formed were filtered, washed, dried and weighed. The results are reported in Table IV.

TABLE IV

INFLUENCE OF ALKALI TREATMENT UPON LIGNIN FROM STRAW AND FROM PEAT

One gram of lignin extracted with 100 cc. of 2% NaOH solution

		Acid lignin from rye straw	Lignin-like complexes from lowmoor peat treated with 2% HCl	Lipin-like complexes from lowmoor peat treated with Et_2O, EtOH and 2% HCl	Lignin-like complexes from highmoor peat treated with Et_2O, EtOH and HCl
24 hrs. cold	**Undis. res., g.**	0.420	0.496	0.420	0.757
	Acid ppt., g.	.428	.292	.428	.057
1 hr. 100°	**Undis. res., g.**	.212	.350	.271	.441
	Acid ppt., g.	.548	.332	.445	.327
30 min. 120	**Undis. res., g.**	.041	.389	.220	.193
	Acid ppt., g.	.663	.405	.523	.534

These results show that acid lignin prepared from rye straw can be dissolved almost completely in 2% sodium hydroxide solution if a sufficiently high temperature and pressure are used.[22] However, only 65 to 75% of the lignin which has been thus dissolved is reprecipitated from the alkali solution on neutralization with hydrochloric acid.

The lignin prepared from peat behaves in this respect very similarly to the lignin of rye straw, with the exception that in this case the amount recovered on acidification is somewhat less.

These results prove further that treatment of rotten wood with a hot alkali solution does not merely remove the oxycelluloses, as assumed by Marcusson, but has a decided effect in bringing the lignin itself, either in an unmodified or in a modified form, into solution.

The possible reason for the discrepancy in the results reported by Rose and Lisse, Bray and Andrews and others, as well as in this paper, on the one hand, and those of Marcusson, on the other hand, may be due to differences in the nature of the organisms concerned in the processes of decomposition. It has been definitely established that under aerobic conditions some fungi and other organisms[2,10a,23,] are capable of attacking

---

[22] M. M. Mehta, Biochem. J., 19, 958–978 (1925).

[23] A. W. Schorger, "The Chemistry of Cellulose and Wood," McGraw-Hill Book Co., New York, 1926.

lignins as well as celluloses. However, under anaerobic conditions no organisms have been found so far which would be capable of decomposing this group of chemical substances. This is largely the reason for the accumulation of lignins under the processes of formation of peat,[20] coal and fossilization of wood, but not in certain aerobic processes of rotting of wood by certain fungi belonging to the group of *Basidiomycetes*.

Although the results presented in this paper are not primarily concerned with the decomposition processes in peat bogs, it may be stated here that evidence will soon be submitted that peat bogs are teeming with life (largely bacterial) and are not sterile, as commonly assumed. The reason for peat formation and its chemical nature as well depend largely upon the nature of these organisms and their activities under anaerobic conditions.

Summary

Decomposition of wood under anaerobic conditions, as in peat bogs or in the process of fossilization, brings about the disappearance of the celluloses and hemicelluloses and a marked accumulation of the lignin complexes.

The nature of the chemical processes involved in the decomposition of wood under aerobic conditions depends largely upon the microorganisms concerned in the process.

There is no justification in assuming that in the decomposition (rotting) of wood, oxycelluloses are formed as an intermediary step in the formation of "humus" from celluloses.

Evidence presented in this paper, as well as by other investigators, definitely establishes the fact that the processes of decomposition of wood are largely microbiological in nature and the nature of decomposition will depend upon the organisms active in the process, as influenced by the environmental conditions and the chemical composition of the plant constituents.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF BENZALDEHYDE AND OF BENZYL BENZOATE

BY CHARLES D. HURD AND C. W. BENNETT

RECEIVED OCTOBER 5, 1928 PUBLISHED APRIL 5, 1929

The pyrolysis of benzaldehyde appears to proceed essentially in one of two directions depending on the conditions of heating. At moderately high temperatures it changes slowly into benzyl benzoate by a polymerization process which involves the double bond of the carbonyl group. At elevated temperatures benzaldehyde rapidly decomposes into carbon monoxide and benzene. These primary effects were reported, respectively, by Lachman[1] and by Peytral,[2] and both appear to be well substantiated. However, certain secondary details in each case seemed open to question, and consequently it appeared expedient to give this subject further study.

A brief summary of the features of our work which contrast with the earlier results follows. Mlle. Peytral passed benzaldehyde vapors rapidly through a short platinum tube at 1150°. We obtained a decomposition similar to hers by using a pyrex combustion tube at 680°. She reported the formation not only of benzene, but also of diphenyl and of a solid, m. p. 213°, stated to be anthracene. Actually, we proved this to be 1,4-diphenylbenzene or "terphenyl," and not anthracene. Its formation is the result of continued pyrolysis of the benzene and diphenyl.

With two hours of heating in a sealed tube at 300°, our results showed much less decomposition of benzaldehyde than Lachman reported. In five such experiments our recovery of unchanged aldehyde was 88–95% as contrasted with 70%. The anticipated pyrolysis occurred, however, at 350–370°. For purposes of comparison, our results obtained at 350–370° are listed in Table I with Lachman's 300° data. Both sets of experi-

TABLE I

PYROLYSIS OF BENZALDEHYDE IN A SEALED TUBE

	Weight of benzaldehyde taken, Lachman, 50 g.		This investigation, 62.5 g.	
Products formed	Moles	Equiv. moles of benzaldehyde consumed	Moles	Equiv. moles of benzaldehyde consumed
Benzyl benzoate	0.01 ± 0.002	0.02	0.073	0.146
Toluene	0.022	0.022	None	None
Benzene	None	None	0.025	0.025
Benzoic acid	0.033	0.033	0.004	0.004
Dibenzyl ether	0.015	0.03	None	None
Total		0.105	....	0.175
Original unrecovered benzaldehyde		0.14	....	0.18
Difference		0.035	....	0.005

---

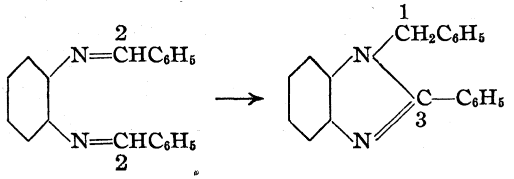
[1] Lachman, THIS JOURNAL, 46,720 (1924).

[2] Peytral, Bull. *soc. chim.*, [4] 29, 44 (1921).

ments were of two hours' duration and in both the recovery of undecomposed aldehyde was about 70%. We found no evidence for toluene or dibenzyl ether as reaction products and only slight evidence for benzoic acid.

From the present data it appears that the essential change at 350–370° is of the Cannizzaro type, giving rise to benzyl benzoate. A minor concurrent reaction, which becomes the major one at higher temperatures, is the pyrolysis into benzene and carbon monoxide.

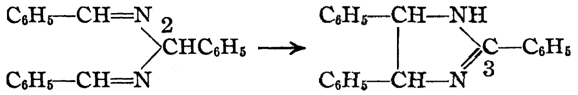
Ammonobenzaldehyde.—Hydrobenzamide and dibenzylidene-o-phenylenediamine may be regarded as analogs of benzaldehyde in the ammonia system. Just as with benzaldehyde, these substances undergo a Cannizzaro type of oxidation and reduction by moderate heating. Dibenzylidene-o-phenylenediamine[3] rearranges into benzaldehydine at 106°.



Atoms numbered (1), (2) and (3) in the equation represent, respectively, carbon atoms in the state of oxidation of alcohol, aldehyde and acid. With benzaldehyde the comparable reaction has been shown to be

$$C_6H_5\text{—}\overset{2}{C}HO + C_6H_5\text{—}\overset{2}{C}HO \longrightarrow C_6H_5\text{—}\overset{3}{C}O\text{—}O\text{—}\overset{1}{C}H_2C_6H_5.$$

Hydrobenzamide undergoes rearrangement[4] into amarine[5] by heating at 130° for three to four hours



Since the high-temperature decomposition of benzaldehyde leads to benzene and carbon monoxide instead of benzyl benzoate, it may be inferred that the high-temperature decomposition of "ammonobenzaldehyde" may also follow quite a different course from that which has just been outlined.

Benzyl Benzoate.—Since benzyl benzoate is a pyrolytic product from benzaldehyde at 350°, it was of interest to study the behavior of benzyl benzoate under similar conditions. The results show that about half of the ester is recoverable after two hours of heating. The products formed

---

[3] Hinsberg and Koller, *Ber.*, 29, 1497 (1896).

[4] Bertagnini, *Ann.*, 88, 127 (1853); Bahrmann, *J. prakt. Chem.*, 27, 296 (1883).

[5] Strain, THIS JOURNAL, 49, 1565 (1927), regarded this change as analogous to the benzoin condensation. That it cannot be analogous is evident from structural difficulties (noted by Strain), and also from the fact that benzoin is not a pyrolytic product of benzaldehyde.

are best explained by assuming an initial disproportionation into benzoic anhydride and dibenzyl ether, the former appearing as such and the latter decomposing[6] further into toluene and benzaldehyde. The reaction mixture was carefully searched for stilbene, phenanthrene, benzene, diphenyl and dibenzyl ether but none of these substances could be identified. The equation, therefore, which best represents the pyrolysis of benzyl benzoate is

$$2C_6H_5COOC_7H_7 \longrightarrow (C_6H_5CO)_2O + [(C_7H_7)_2O]$$
$$[(C_7H_7)_2O] \longrightarrow C_6H_5CHO + C_6H_5CH_3$$

A small amount of benzoic acid, in addition to the benzoic anhydride, was also formed. It may have been produced as a primary product, or it may have been produced secondarily from the benzoic anhydride or the benzaldehyde. At least, the absence of stilbene may be taken as evidence that phenylmethylene, $[C_6H_5CH=]$, did not appear even momentarily. Phenylmethylene is the residue obtained by detaching the elements of benzoic acid from benzyl benzoate. Possibly some of the benzaldehyde may have arisen by reversal of the Cannizzaro reaction, but the fact that toluene and benzaldehyde were isolated in roughly equivalent quantities is contra-evidence.

Esters with β-hydrogens in the alcohol part of the molecule, such as $RCO_2CR_2CHR_2$, are known to pyrolyze readily into acid, RCO_2H, and olefin, $R_2C=CR_2$. Benzyl benzoate has no such β-hydrogens and in this respect it is similar to methyl benzoate and benzohydryl benzoate. The former[7] of these is stable to 400°, but the latter[8] gives benzoic anhydride (among other things) on distillation. Presumably the primary effect is one of disproportionation.

$$2C_6H_5CO_2CH(C_6H_5)_2 \longrightarrow (C_6H_5CO)_2O + [((C_6H_5)_2CH)_2O]$$

Experimental Part

Benzaldehyde at 300–310°.—Benzaldehyde was freshly distilled *in vacuo* and was collected over a 2° range. About 50-g. portions were placed in pyrex bomb tubes. Air was excluded with benzaldehyde vapors by boiling prior to sealing. The tube was heated in a bomb furnace for two hours at 300–310° and left overnight to cool. Five such runs were made and the greatest non-recovery of benzaldehyde was 7 g. from 62 g. The percentage of recovery varied between 88–95%. Benzyl benzoate was the major product in the non-benzaldehyde portion, but there was always a small amount of benzoic acid. In no case was any other product isolated.

Pyrolysis of Benzaldehyde at 350–370°.—The details of a characteristic experiment will be related. A sample of benzaldehyde weighing 62.5 g. (freshly vacuum distilled)

---

[6] Benzoic anhydride is known to be stable at least to 400° [Anschiitz, Ber., 10, 1883 (1877); *Ann.*, 226, 15 (1884); Deninger, J. *prakt.* Chem., 50, 480 (1894); Staudinger, Ber., 44, 544, footnote (1911)], whereas dibenzyl ether decomposes rapidly at its boiling point, 295°, and slowly at 210–215° [Cannizzaro, *Ann.*, 92, 113 (1854); Lowe, *ibid.*, 241, 374 (1887); Lachman, THIS JOURNAL, 45, 2358 (1923)].

[7] Engler and Low, *Ber.*, 26, 1441 (1893).

[8] Linneman, *Ann.*, 133, 23 (1865); Anschiitz, *ibid.*, 235, 220 (1886).

was heated for two hours in a sealed tube at 350–370°. After cooling overnight and opening, considerable pressure of an inflammable gas was noted. On distillation of the red liquid, 30 g. was obtained from 110–176°, which, on redistillation, yielded 2 g. of a mobile liquid between 70 and 120°. This was chiefly benzene, as shown by nitration to dinitrobenzene (m. p. 88–89°) and confirmation by a mixed melting point determination with a known sample of dinitrobenzene. The mixture melted also at 88–89°. From this first fraction, and from that boiling from 176–196°, 43 g. of benzaldehyde was recovered. Half a gram of benzoic acid was extracted from the residue, thereby leaving 15.5 g. of a benzyl benzoate portion, b. p. 130–190° (6 mm.), and 1 g. of brown residue.

Fifteen g. of the 15.5 g. of liquid just mentioned, on hydrolysis with alcoholic potassium hydroxide (reflux one hour), gave 7 g. of benzyl alcohol, b. p. 75–80° (6 mm.) and 8.4 g. of benzoic acid. The theoretical yields for 15 g. of benzyl benzoate would be 7.6 g. of the alcohol and 8.6 g. of the acid. There was no high boiling residue and no indication of dibenzyl ether.

Pyrolysis of Benzaldehyde at 680–690°.—Forty-one g. of benzaldehyde was dropped from a stoppered-in dropping funnel into an upturned elbow of a nitrogen-filled pyrex combustion tube. The tube was about a meter long and was maintained at 680–690° (thermocouple measurement) by an electric furnace. The effluent end of the tube was connected to a smaller tube which led through a condenser into a receiving flask. The outlet of the flask was connected so that the gas formed could be collected over a saturated sodium chloride solution. After four hours all the benzaldehyde was added. Therefore, the rate of entry was $^1/_6$ g. per minute. The distillate weighed 31 g. and the volume of the gas was 5.8 liters (standard conditions).

The 31 g. of liquid, on fractionation, gave 11 g. of benzene, 13.5 g. of benzaldehyde and 2.5 g. of diphenyl. Diphenyl (m. p. 65°) was positively identified by chemical and physical properties. From the fraction boiling at 150–200° at 18 mm. about 0.3–0.5 g. of a white crystalline solid (m. p. 213°, corr.) was obtained after two crystallizations from alcohol. It was easily sublimed when distilled in a vacuum and was practically insoluble in cold alcohol or ether. It appeared to be the "anthracene" which Peytral found at 1150°, but no anthraquinone could be isolated from a chromic acid oxidation of a portion, nor could a picrate be made. A mixed melting point determination with anthracene (m. p. 210°) gave a melting point at 170°. Thus the substance was not anthracene. These properties are all those of "terphenyl" or 1,4-diphenylbenzene. In confirmation, a mixed melting point with a known sample of the latter showed no depression of the melting point; mixed m. p. 213° (corr.). Also, it dissolved characteristically in sulfuric acid with a green-blue color which changed to purple on boiling. Finally, a small amount of white powder which did not melt below 295° (terephthalic acid) was obtained from the chromic acid oxidation mixture.

The gas (5.8 liters, corrected volume) contained no methane or unsaturated hydrocarbons. By volume it analyzed as follows: carbon monoxide, 86.7%; hydrogen, 12.9%; carbon dioxide, 0.32%. This is calculated to a nitrogen-free basis.

Benzyl Benzoate, Preparation.—Benzyl benzoate was prepared by refluxing benzoyl chloride and benzyl alcohol for three hours by the method of Cannizzaro.[9] The yield of ester (alkali washed, and b. p. (23 mm.) 198–203°) was found to be 44.5%.

Pyrolysis of Benzyl Benzoate at 350°.—A sample of the ester weighing 42.5 g. (b. p. (21 mm.) 193–198°) was sealed in an evacuated tube and kept at 340–350° for two hours. After cooling overnight, the tube was opened and found to contain an apparently non-combustible gas under high pressure. The contents were black and the volatile portions were distilled off. Three g. of toluene and 2 g. of benzaldehyde

---

[9] Cannizzaro, *Ann.*, 90, 254 (1854).

were isolated. The toluene was identified as dinitrotoluene, which melted at 68–70" after two recrystallizations from alcohol. The same derivative similarly prepared from pure toluene melted at 69–70°, and a mixed melting point was 68–70°. The less volatile material was distilled under diminished pressure, thereby yielding 31.5 g. of distillate. It was dissolved in ether and extracted with alkaline solution, thereby removing 2 g. of benzoic acid. Test portions of the mixture absorbed bromine without the evolution of hydrogen bromide. Although indicative of unsaturated hydrocarbons such as stilbene, no such dibromide could be found. Actually the bromine absorption was caused by benzoic anhydride.[10] A known sample of benzoic anhydride behaved identically. The unused portion weighed 24.5 g. and 20 g. of this was saponified by refluxing with alcoholic potassium hydroxide for an hour and a half. This produced 7.5 g. of benzyl alcohol, b. p. (6 mm.) 75–80". The equivalent quantity of benzoic acid would be 8.5 g. but actually 12 g. (m. p. 120–122°) was isolated. The excess was produced from benzoic anhydride. These data indicate at least 15 g. of benzyl benzoate and about 3 g. of benzoic anhydride in the original 20 g. which was saponified. In terms of the 31.5 g. of distillate, this extrapolates to 23.6 g. of benzyl benzoate and 4.7 g of benzoic anhydride.

Summary

The decomposition of benzaldehyde is very slow at 300°, but about one-third of it decomposes, largely into benzyl benzoate, in two hours at 350°. A concurrent reaction of much less importance gives rise to carbon monoxide and benzene. No evidence could be obtained for toluene or dibenzyl ether as reaction products and benzoic acid is formed in negligible amounts.

By passing benzaldehyde through a pyrex tube at 700° at a rate of one-sixth g. per minute, it was about two-thirds decomposed. The major reaction was the formation of benzene by loss of carbon monoxide. Side reactions gave rise to diphenyl and 1,4-diphenylbenzene. Anthracene was definitely absent.

At 350" benzyl benzoate undergoes a reaction of disproportionation. After two hours' heating, the major products of change are benzoic anhydride, toluene and benzaldehyde. Smaller amounts of benzoic acid were also indentified. Negative searches were made for stilbene, phenanthrene, benzene, diphenyl and dibenzyl ether in the products of reaction.

EVANSTON, ILLINOIS

---

[10] Gal, *Compt.* rend., 54, 1228 (1862).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

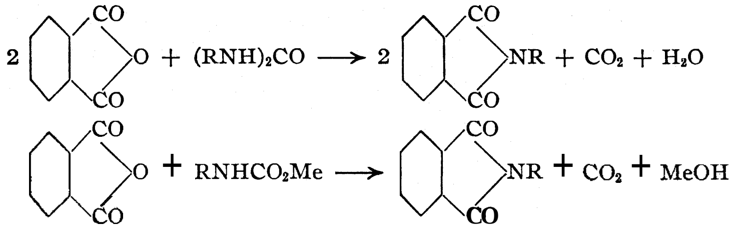
A MODIFICATION OF THE CURTIUS SYNTHESIS OF PRIMARY AMINES

BY RICHARD H. F. MANSKE[1]

RECEIVED OCTOBER 23, 1928 PUBLISHED APRIL 5, 1929

The usefulness of the Curtius reaction for the synthesis of primary amines is considerably decreased because of the difficulty frequently encountered in hydrolyzing the intermediate alkylureas and urethans. Di-p-phenylethylurea is hydrolyzed completely only after prolonged heating in a sealed tube with concentrated hydrochloric acid at high temperatures.[2] Such a procedure is likely to result in dealkylation when alkoxyl groups are present. The author observed that di-β-(3-indolylethyl)-urea was completely resinified on heating with hydrochloric acid even for a short time, while boiling with saturated alcoholic potassium hydroxide for twenty-four hours resulted in no change. Distillation with soda lime is generally to be avoided and is obviously too drastic in this case. The high temperature is conducive to decomposition and the yield of impure product is frequently very low.

When alkylureas are heated with phthalic anhydride, alkyl phthalimides are formed in excellent yield,[3] and the same reaction has now been applied to alkyl urethans. The reactions are represented as follows



and bring the methods of Gabriel and of Curtius into a common field. The subsequent hydrolysis of the alkylphthalimides may be quantitatively accomplished by the reaction of Ing and Manske.[4]

The examples described in the experimental section suffice to illustrate the generality of the reaction here discussed.

Experimental

1,8-Diphthalimido-octane.—A mixture of octamethylene-1,8-dimethylurethan[5] (4 g.) and phthalic anhydride (8 g.) was heated in an oil-bath at 230° until evolution of gases ceased (*ca.* thirty minutes). The reaction mixture which contained a small

---

[1] Eli Lilly Research Fellow, Yale University, 1927–1928–1929.

[2] Thiele and Pickard, *Ann.*, 309, 200 (1899).

[3] Tingle and Brenton, THIS JOURNAL, 32, 116 (1910).

[4] Ing and Manske, *J. Chem. Soc.*, 2348 (1926).

[5] Steller, *J. prakt. Chem.*, [2] 62, (a) 224, (b) 226 (1900).

amount of phthalic anhydride was cooled to 100°, treated with a small volume of alcohol and then neutralized with an excess of aqueous sodium bicarbonate. The precipitated diphthalimide compound crystallized almost at once. It was filtered off, thoroughly washed with water, dried and recrystallized from a small volume of alcohol, in which it is moderately soluble; yield, 7.4 g. It consists of colorless, glistening needles melting at 138°.[6]

Anal. Calcd. for $C_{24}H_{24}O_4N_2$: N, 6.93. Found: N, 6.43, 6.71.

In order to confirm the identity of this product a small amount was hydrolyzed with hydrazine hydrate.[4] The hydrochloride of the resulting base was identical in all respects with an authentic specimen of octamethylenediamine hydrochloride (mixed m. p. 277°).[5b]

Di-γ-phenoxypropylurea.—γ-Phenoxybutyric hydrazide, $C_6H_5OCH_2CH_2CONH\text{-}NH_2$, was prepared by heating a mixture of 70 g. of ethyl y-phenoxybutyrate, 20 g. of hydrazine hydrate (90%) and 50 cc. of ethyl alcohol under a reflux for ninety minutes. The greater portion of the alcohol was removed by distillation and the residue was heated under reflux for sixty minutes more. The cooled mixture yielded 55 g. of hydrazide which after two recrystallizations from alcohol had a melting point of 81–82°.

The crude hydrazide was converted into the azide by treating an iced solution of 19.4 g. in 200 cc. of water and 10 cc. of concentrated hydrochloric acid with 6.9 g. of sodium nitrite. The precipitated azide was thoroughly washed with iced water (it melted at room temperature to *a* pale yellow liquid) and decomposed by gradually heating it in 50 cc. of acetic acid and 300 cc. of water. The urea crystallized even while the liquid was boiling. It was filtered off, washed with water and recrystallized from alcohol, in which it is only sparingly soluble. The yield of purified product was 10 g. After another recrystallization from alcohol (charcoal) it melted sharply at 150°.

Anal. Calcd. for $C_{19}H_{24}O_3N_2$: N, 8.54. Found: N, 8.47.

γ-Phenoxypropylphthalimide.—Di-γ-phenoxypropylurea (16.4 g.) was heated with phthalic anhydride (16 g.) at 225° in an oil-bath until evolution of gases ceased (fifteen minutes). The excess phthalic acid was removed with aqueous sodium bicarbonate and the alkyl phthalimide recrystallized from alcohol; yield of pure product, 24 g. It melted alone or admixed with an authentic specimen at 91°.[7] Hydrolysis with hydrazine hydrate[4] yielded γ-phenoxypropylamine hydrochloride melting at 168° (alone or admixed with an authentic specimen).'

β-(3-Indolylethyl)-phthalimide, $(C_8H_6N)CH_2CH_2N(CO)_2C_6H_4$.—In the course of some experiments with the azide of indolylpropionic acid,[8,9] a small yield of di-β-(3-indolylethyl)-urea was frequently encountered. The exact conditions for obtaining this urea in good yield have not been investigated sufficiently and this subject together with some further work on indolylpropionic and indolylbutyric acids will form the substance of an early communication.

When the urea was heated at 225° with an excess of phthalic anhydride and the mixture worked up in the usual way, the phthalimide was obtained in excellent yield. After two recrystallizations from alcohol (charcoal) it consisted of pale yellow needles (readily soluble in hot alcohol) melting at 164–165°.

Anal. Calcd. for $C_{18}H_{14}O_2N_2$: C, 74.48; H, 4.83. Found: C, 74.32; H, 4.96.

On hydrolysis with hydrazine hydrate it produced tryptamine (β-3-indolylethyl-

---

[6] Melting points are corrected.

[7] Lohmann, *Ber.*, 24, 2634 (1891).

[8] Manske and Robinson, J. *Chem. Soc.*, 240 (1927).

[9] Kalb, Schweizer and Schimpf, *Ber.*, 59, 1858 (1926).

amine) in quantitative yield. The hydrochloride consisted of colorless needles melting at 248°. The picrate had a melting point of 243°.[10]

Summary

1. It is suggested that the hydrolysis of alkylureas and urethans, when acid or alkali hydrolysis is impracticable, be accomplished by means of phthalic anhydride and subsequently with hydrazine hydrate.
2. This procedure has been utilized in the synthesis of tryptamine.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DYE LABORATORY OF THE CHEMISTRY DIVISION OF THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

THE RELATION BETWEEN THE ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF CERTAIN AZO DYES. I. THE EFFECT OF POSITION ISOMERISM ON THE ABSORPTION SPECTRA OF METHYL DERIVATIVES OF BENZENE-AZOPHENOL[1,2]

BY WALLACE R. BRODE

RECEIVED OCTOBER 27, 1928 PUBLISHED APRIL 5, 1929

The effect of position isomerism on the absorption spectra of similarly constituted aromatic compounds has been studied by Baly,[3] Purvis,[4] Klingstedt[5] and Henri[6] together with their co-workers in this field. In general it has been shown that substitution in the para position produces a stronger absorption band than substitution of the same group in either the ortho or meta position in the benzene ring. This effect, although not always mentioned, can be noted in the data of other observers. Recent work by Henri on the absorption spectra of isomeric xylenes and dihalogenated benzene compounds in the vapor phase has shown considerable variation in the fine structure of the absorption bands with a change in the position of substitution. The unstable nature of azo dyes, however, does not permit the study of their absorption spectra in a vapor state, so that data by this method are unobtainable on the compounds studied in this paper.

The object of this investigation is a fundamental quantitative study

---

[10] Ewins, J. *Chem. Soc.*, **99**, 270 (1911).

[1] Publication approved by the Director of the National Bureau of Standards, Department of Commerce.

[2] Presented in part at the Philadelphia meeting of the American Chemical Society in September, 1926.

[3] Baly, J. *Chem. Soc.*, **107**, 1058 (1915).

[4] Purvis, *ibid.*, **103**, 1088 (1913).

[5] Klingstedt, *Compt. rend.*, **175**, 365 (1922).

[6] Henri, "Structure des Molécules," Herman, Paris, **1925**, and unpublished data communicated to the author.

of the relation between the absorption spectra and chemical constitution of simple derivatives of benzene-azophenol. The isomeric series of dyes selected for this study include, together with the parent substance, benzene-azophenol, all the possible mono- and dimethyl derivatives of benzene-azophenol in which not more than one methyl group occurs in a benzene ring. These dyes, prepared from c.p. intermediates, were recrystallized several times from alcohol and analyzed according to the Kolthoff[7] modification of the Knecht and Hibbert[8] titanous chloride titration method for azo dyes (see Table I).

Experimental

The data presented in this paper deal only with these dyes dissolved in a 3% aqueous solution of sodium hydroxide.[9] The alkaline dye solutions for spectrophotometric examination were prepared as follows.

The weighed amount of dye, 0.7200 g. of benzene-azophenol or 0.8450 g. of its various mono- and dimethyl derivatives, was dissolved in 500 ml. of alcohol (95%) at 20°. Fifty ml. of this solution were diluted to 250 ml. with alcohol and then 10 ml. of this latter solution and 10 ml. of a 30% solution of c.p. stick sodium hydroxide in distilled water were diluted to 100 ml. with distilled water. Thus the solutions which were measured contained 2.880 cg. per liter of benzene-azophenol or 3.380 cg. per liter of the mono- and dimethyl derivatives. It should be noted that the solutions as used contained a small amount of alcohol.

The experimental observations were made with a Hilger sector photometer and spectrograph.[10] This apparatus and the system of nomenclature used in the presentation of the data are described in previous papers published in THIS JOURNAL and elsewhere.[11] The data presented are plotted with $-\log_{10}$ transmittancy (intensity of absorption) as the ordinates and frequency in vibrations per 10^{-12} second as the abscissas. In Figs. 1 and 2 the concentrations are the same only when the molecular weights of the compounds are the same. In Table I, however: the absorption values have been corrected for analysis and weight so that all of the indicated values are for the same molecular concentration, that is, 1.5×10^{-4} g. mole per liter. The cell thickness used in all cases was 0.5 cm.

Discussion of Data

An examination of the absorption curves, Figs. 1 and 2, will show that all of these compounds exhibit the same general type of absorption.

---

[7] Kolthoff, *Rec. trav. chim.*, **45,** 169 (1926).

[8] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, New York, 1925.

[9] The absorption spectra of these dyes have also been measured in 95% ethyl alcohol and in concentrated (35%) hydrochloric acid as solvents. For data in these solvents and a more extended presentation of the effects of the sodium hydroxide solvent see a forthcoming paper in the *Bureau of Standards Journal of Research.*

[10] Placed at the author's disposal by the Colorimetry Section of the Bureau of Standards.

[11] (a) Gibson and others, *J. Opt. Soc. Am., 10,* 169 (1925); (b) Gibson and others, *Bureau of Standards Sci. Papers 440,* **18,** 121–184 (1922); (c) Brode with Adams, THIS JOURNAL, **46,** 2033 (1924); (d) Brode, *J. Phys. Chem., 30,* 56 (1926); (e) Brode, THIS JOURNAL, **48,** 1984 (1926).

TABLE IA

THE INTENSITIES OF THE ABSORPTION BANDS OF THE COMPOUNDS STUDIED IN A 3% AQUEOUS SOLUTION OF SODIUM HYDROXIDE

(Values given in $-\log_{10}$ transmittancy.) Concentration, 1.5×10^{-4} gram mole per liter; cell thickness, 0.5 cm.

Compound		Anal. by $TiCl_3$, %	M. p., °C. (obs.)	M. p., °C. (lit.)[b]	Cg. per liter of pure dye ≡ to 1.5×10^{-4} mole per liter
Benzene-azophenol	(Ph)[a]	99.6	152	152	2.971
Benzene-azo-*o*-cresol	(*o*)	99.2	128	128–130	3.182
Benzene-azo-m-cresol	(m)	98.5	107	109	3.182
o-Toluene-azophenol	(o')	99.5	102	102–3	3.182
m-Toluene-azophenol	(m')	98.3	140	144–5	3.182
p-Toluene-azophenol	(p')	100.8	151	151	3.182
o-Toluene-azo-o-cresol	(o'-o)	99.6	132	132	3.392
o-Toluene-azo-m-cresol	(o'-m)	100.5	113	111	3.392
m-Toluene-azo-o-cresol	(m'-o)	98.0	114	115	3.392
m-Toluene-azo-m-cresol	(m'-m)	99.5	106	106–7	3.392
p-Toluene-azo-o-cresol	(*p'-o*)	100.2	162	163	3.392
p-Toluene-azo-m-cresol	(p'-m)	99.7	135	135	3.392

[a] These abbreviations are used in Figs. 1 and 2 as well as other parts of this paper to designate these compounds.

[b] Beilstein, "Handbuch der organischen Chemie," Vol. IV, Ergänzungsband (1906)

TABLE IB

THE MAGNITUDE OF THE ABSORPTION BANDS OF THE COMPOUNDS STUDIED IN A 3% AQUEOUS SOLUTION OF SODIUM HYDROXIDE

Absorption bands		I				II
A (obs.)	*B* (obs.)	A' (anal.)	*B'* (anal.)	A' + *B'*	*A'/A' + B'*	
1.70	1.56	1.53	1.29	2.82	0.543	0.60
1.84	1.38	1.82	0.85	2.67	.682	.68
1.55	1.67	1.38	1.29	2.67	.518	.65
1.48	1.63	1.18	1.40	2.58	.457	.61
1.69	1.55	1.50	1.26	2.76	.543	.66
1.77	1.60	1.57	1.32	2.89	.542	.66
(1.63)[a]	(1.51)[a]	1.47	1.06	2.53	.581	.65
1.14	1.63	1.06	1.34	2.40	.442	.61
1.96	1.50	1.92	0.90	2.82	.680	.71
1.53	1.71	1.40	1.31	2.71	.517	.61
2.05	1.26	2.05	1.02	3.07	.668	.72
1.64	1.86	1.52	1.42	2.94	.517	.73

[a] Approximate values.

There is a strong band between 670 and 750 f. and a weaker one between 1125 and 1200 f. The principal band is slightly asymmetric in form, the lower frequency side having a steeper slope than the higher frequency side. Further it is markedly deformed in the region of maximum absorption. Apparently it is composed of two overlapping bands. These components appear to be in equilibrium with each other, for where one of them is increased the other is diminished in intensity (see Table I). This suggests the presence of two slightly different modifications of the compounds in the solutions studied, the proportions of **which** are influenced by the position of the substituting group.

From a study of the absorption bands of these **and** similar compounds in various other solvents,[9,11d,11e] it may be seen that in any one solvent,

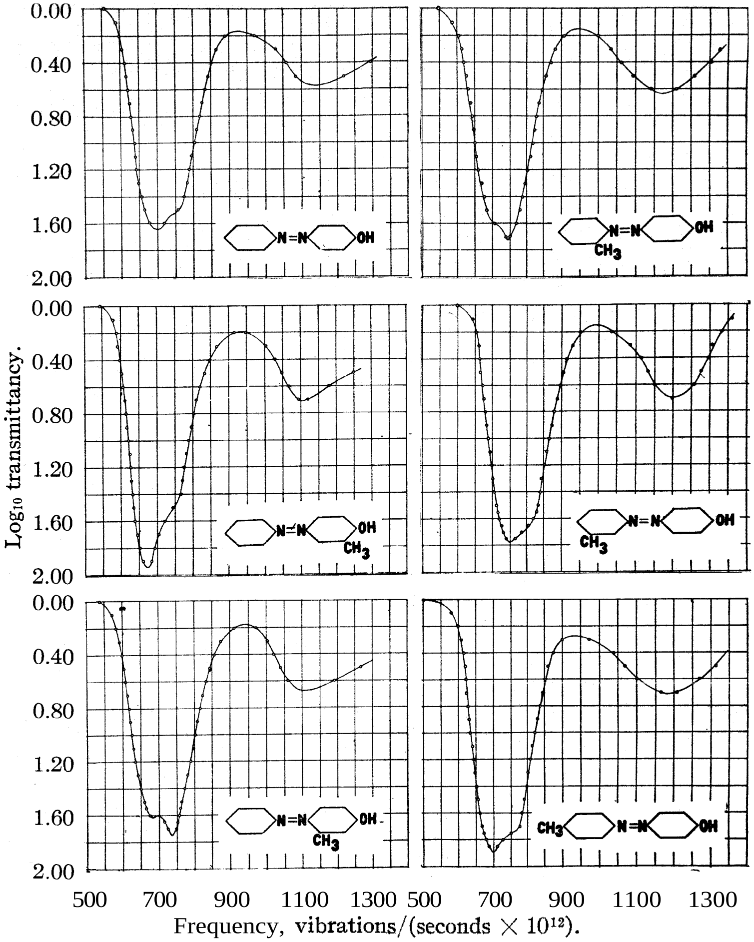


Fig. 1.—The absorption spectra of benzene-azophenol and its monomethyl derivatives in a 3% aqueous solution of sodium hydroxide. Concentration: benzene-azophenol, 2.88 cg. per liter; the monomethyl derivatives, 3.38 cg. per liter; cell thickness in all cases 0.5 cm. Top left, (Ph); top right, (*o'*); middle left, (*o*); middle right, (m'); lower left, *(m);* lower right, (*p'*). For explanation of symbols, see Table I.

although the intensity or frequency may be shifted, the mathematical relation between the bands and their general shape when calculated to the same intensity of absorption is the same. Assuming that the two bands which make up the principal band in Figs. 1 and 2 have the same shape in all cases, an analysis of the curves into these components is possible and only one set of curves answering this requirement can be constructed.[12] It is found that approximately the same mathematical

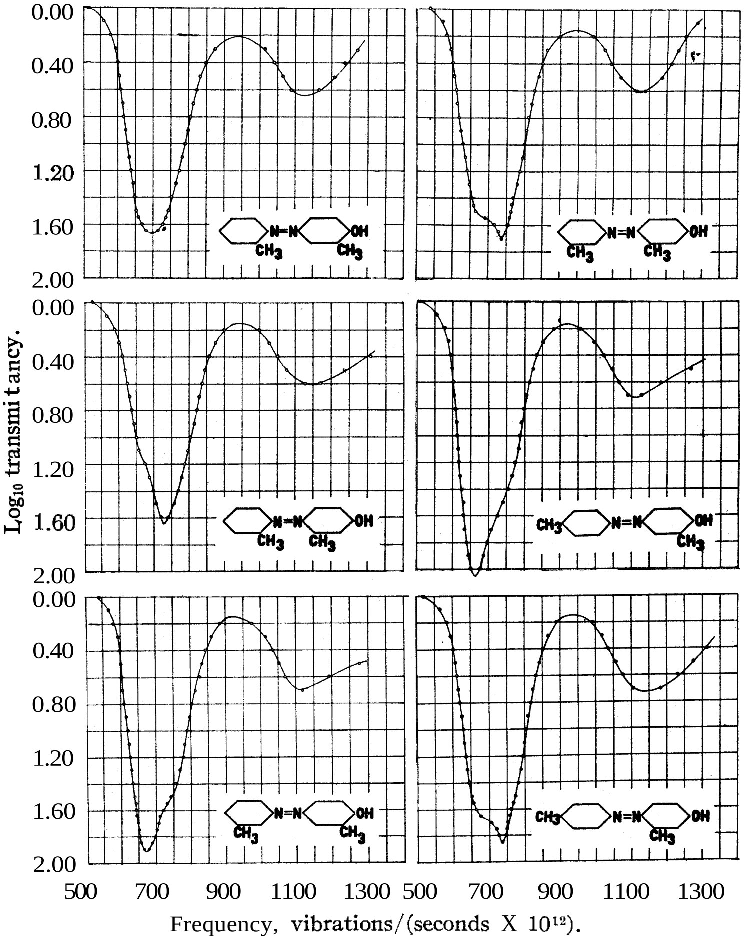


Fig. 2.—The absorption spectra of dimethyl substituted derivatives of benzene-azophenol in a 3% aqueous solution of sodium hydroxide. Concentration: **3.38** cg. per liter; cell thickness, 0.5 cm. Top left, (*o'-o*); top right, (*m'-m*); middle left, (o-m); middle right, (*p'-o*); lower left, (*m'-o*); lower right (*p'-m*). For explanation of symbols, see Table I.

relations with regard to frequency exist between the components of the principal bands. These facts tend to justify the assumption that the curves are composed of but two similar components. Whether or not

---

[12] Brode, Proc. Roy. *Soc.* London, **118A,** 290 (1928).

this assumption is true, their shape gives that appearance and the data obtained by the analysis afford a better expression of the changes in the principal bands than the curves themselves.

In Table I are given both the observed and calculated values of the components of the principal absorption bands. The observed values are indicated by A and B, corresponding to the low and high frequency

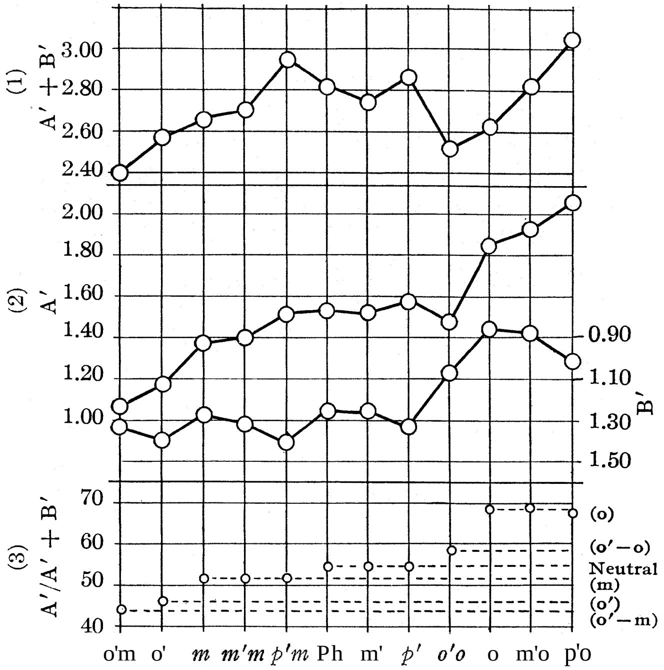


Fig. 3.—(1) Absorption intensities of the sum of the component bands (A' + B') of the principal band observed in a 3% aqueous solution of sodium hydroxide. Concentration, 1.5×10^{-4} mole per liter; cell thickness, 0.5 cm. Abscissas in $-\log_{10}$ transmittancy. (2) Absorption intensities of the principal band observed in a 3% solution of sodium hydroxide. A' = upper series, B' = lower series. Abscissas in $-\log_{10}$ transmittancy. (3) Percentage of the A' component of the principal band in a 3% aqueous solution of sodium hydroxide. (The abbreviated symbols for the compounds are explained in Table I.)

components, respectively, and the calculated values are similarly designated by A' and B'. It may be seen that the general direction of the deviations is the same in both cases. Fig. 3 (1) gives the sum of the absorption values of the components (A' + B'). As has been noted in other solvents and compounds, substitution in the *p'*-position results in an increase in the intensity of the absorption bands and this generalization holds equally true in the case of aqueous sodium hydroxide as a solvent. Also substitution in the o'-position tends to decrease the intensity of the bands as well as to influence the ratio between the A and B components.

In the absorption spectrum of benzene-azophenol, the parent substance of this series, in an aqueous solution of sodium hydroxide, there is what we may call a neutral equilibrium, in which band A is slightly more intense than band B. This neutral equilibrium does not represent an equal amount of the two forms and may undoubtedly be influenced by changes in the character of either the basic substance or the solvent.[9] For example, in the absorption spectrum of benzene-azophenol in an alcoholic solution of sodium hydroxide, the equilibrium has been shifted, with an increase in B and a corresponding decrease in A. Two other curves closely resemble the neutral curve of benzene-azophenol, namely, those of the *m'*- and *p'*-substituted compounds (Fig. 1). These two, together with the unsubstituted parent substance, constitute the neutral group or series. In the case of the *m'*-substituted compounds, there appears to be practically no effect of any kind on either the equilibrium or the intensity of the A and B bands. In the case of the *p'*-substituted compounds there is an increase in the intensity of absorption, but the relative shapes of the bands and the ratio between the components A and B are the same as in the original compound without the p'-substitution.

Substitution in the o-position (ortho to the hydroxyl group) (Fig. 1) causes a marked increase in the A band and a corresponding decrease in the B band or, in other words, a shift of the equilibrium toward the A state.

Substitution in the m-position (meta to the hydroxyl group) causes a shift of the equilibrium in the opposite direction, that is, an increase in the B band with a corresponding decrease in the A band. The degree of shift of this equilibrium from the neutral state, however, is not as great as in the case of the o-substitution.

Substitution in the o'-position causes an increase in the B component with a corresponding decrease in the A component, producing a relation differing from the neutral ratio by about the same amount, but in the opposite direction, as that caused by the o-substitution. In addition there is a suppression of both bands so that the sum of the intensities of A and B is considerably smaller than in the other cases (Fig. 3 (1)).

The general effect of disubstitution on the intensities of the two component bands is a combination of the effects produced by the two separate directing forces. In the case of the *o',o*-substituted compound (Fig. 2) the effects of the two substituting groups are opposite in character and to a large extent neutralize each other. The o-substitution appears to have a slightly stronger influence than the o'-substitution as the intensity of the A component present is slightly greater than in the neutral equilibrium. The effect of the o'-substitution, however, on the suppression of the bands seems to be only slightly influenced by the oppositely directed force of the o-substitution. In the o^1,m-substituted compound the substituting positions influence in the same direction from the neutral equilibrium or level, so that there is an addition of the two effects and a slightly greater suppression of the bands, due to the o-substitution. The effect of the introduction of the second substitution in the *m′*-position on the absorption spectrum of the compound is practically nil within the accuracy of the observations. There is possibly a slight increase in the intensity of the bands of the m^1,o-substituted compound above those of the o-substituted compound alone and a slight lowering of the ratio of A to B. In the absorption spectrum of the *m′*,*m*-substituted compound there is an indication of the same effect, although it is less prominent than in the *m′*,*o*-substituted compound. The influence of the substitution in the *p′*-position, as mentioned before, seems to be merely to increase the intensity of absorption, an effect quite independent of the solvent used.

In the graph (Fig. **3** *(2))* giving the intensities of absorption of components A' and B', those of B' are plotted on an inverted scale, since from general observation it may be seen that as one band increases the other decreases. It is to be noted that in cases which are normal, such as the unsubstituted, m-substituted and m^1-substituted compounds, approximately the same differences exist between the A′ and B′ values in the graph. Cases in which there is an intensification of the bands, *p′*-substituted compounds, show a difference greater than normal values, and cases with suppressed bands, o-substituted compounds, show differences smaller than the normal values.

A comparison of the sums of the calculated values of the intensities of the A' and B' bands (Fig. **3** (1)) with those of the principal bands of these same compounds in other solvents[8] shows that the same general relations exist in regard to the intensities of the absorption bands. This lends confirmation to the theory that, in any particular compound, the equilibrium between the concentration of the tautomeric forms represented by the bands A and B is directly proportional to the intensities of their absorption bands (A^1 and B').

The ratio of A′ to (A' + B') should, therefore, give approximately the percentage of the (A) tautomeric compound present and at the same time make the necessary corrections or allowances for the *p′*- and *o′*-effects on the intensities of both the component bands. (Fig. 3 (3)) gives these percentage values which, as may be observed, can be arranged in groups representing different stages or levels in the equilibrium. The highest percentage is about 68% of the A compound, which may be called the o-level. The next stage is that of a neutralized effect from two different levels which exert their influences in opposite directions from the neutral level; this is the combined effect of the o- and o'-substituting groups. The influence of the o-substitution is apparently somewhat stronger than that of the 0'-substitution, so that the level of this stage is still above the neutral level.

The next level is that of neutrality and is at about 55% of A under the conditions observed. As has been mentioned before, the use of other solvents for the alkaline reagent may shift this level or equilibrium. In the neutral level are the mono-substituted, *m'*- and *p'*-compounds, as well as the parent substance.

The effect of the m-substitution is not as strong as that of either the o- or the 0'-substitution. In the cases observed the equilibrium level has been lowered to about 51% of A.

The o'-substituted compound, when not influenced by other substitutions, produces an equilibrium at about 44% of A. The effect of the *o*-substitution on the 0'-substituted compound has been mentioned, and in the case of the *o'*,*m*-disubstituted compound, where both groups tend to lower the percentage of A in the equilibrium, the effect is additive, giving an equilibrium level at 41% of A.

The author wishes to express his appreciation of the help and suggestions given by W. D. Appel of the Dye Laboratory of the Bureau of Standards.

Summary

Benzene-azophenol and the eleven possible mono- and dimethyl derivatives, in which not more than one methyl substitution occurs in a benzene ring, have been prepared and their absorption spectra measured in a 3% aqueous solution of sodium hydroxide in the visible and ultraviolet regions of the spectrum to about 1250 to 1400 f.

From these data the following generalizations have been made.

1. The principal absorption bands appear to be composed of two component bands which, added together, produce the observed bands.

2. The equilibrium between the two components of a band is dependent on the nature of the solvent and the position of the substituting group. An o-substitution of the methyl radical in the benzene-azophenol molecule results in an increase in the lower frequency component, with a corresponding decrease in the higher frequency component. A m- or o'-substitution produces a reverse effect, while the equilibrium is not affected by either a m'- or *p'*-substitution.

3. Substitution of a methyl radical in the *p'*-position in benzene-azophenol causes an increase in the intensity of the absorption bands, irrespective of the type of solvent.

4. Substitution of a methyl radical in the 0'-position in benzene-azophenol causes a decrease in the intensity of the absorption bands.

The data suggest the possibility of a method of structural analysis for the determination of the position of a substituting group in a complex molecule, and a reverse of this in the prediction of the absorption spectra of compounds of known formula and structure. Additional data on the effects of substituting groups, including those of nitro,[13] chlorine and bromine substitutions, are now being collected with this object in view.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A METHOD FOR THE QUANTITATIVE ANALYSIS OF TIM IN ORGANIC COMPOUNDS

BY HENRY GILMAN AND W. BERNARD KING

RECEIVED OCTOBER 29, 1928 PUBLISHED APRIL 5, 1929

Introduction

In connection with studies on organotin compounds a need was felt for a convenient method for the quantitative estimation of total tin. The successful method described recently by Gilman and Robinson[1] for the estimation of total lead in organolead compounds suggested a similar technique for the analysis of tin. That method, applied to non-volatile organolead compounds, involved decomposition with concentrated sulfuric and nitric acids in the open. It was soon found to be without value when applied to a variety of alkyl tin compounds because of loss due to spattering and volatilization. We have shown that the method is applicable to the analysis of essentially non-volatile organotin compounds, and prior to our analytical studies Krause and Becker[2] used fuming sulfuric and fuming nitric acids for the analysis of some *aryl* tin compounds.

The obvious convenience of carrying out the analysis in open dishes directed efforts to find reagents that would decompose *all* organotin compounds without risk of losing any of the sample as a consequence of spattering or volatility due to vigorous decomposition incidental to the formation of stannic oxide. Several reagents were tried.[3] A satisfactory

---

[13] Brode, *Ber.*, 61, 1722 (1928).

[1] Gilman and Robinson, THIS JOURNAL. 50,1714 (1928).

[2] Krause and Becker, *Ber.*, 53, 178 (1920). In an article which has just appeared, Fichter and Herzbein, *Helv. Chim. Acta*, 11, 562 (1928), analyzed tin dichlorodiacetate by hydrolyzing the aqueous solution of the compound with ammonia and ammonium nitrate.

[3] One of these involved a *preliminary* decomposition by concd. hydrochloric acid, followed by the nitric–sulfuric acid oxidation to stannic oxide. In this method the compound is first dissolved in carbon tetrachloride, which is an excellent solvent for organotin compounds. The preliminary decomposition by hydrochloric acid is slower than the preliminary decomposition by bromine. However, satisfactory results were obtained by this method with the few compounds tried. We prefer the bromine method that is more fully described in this paper

reagent for non-volatile tin compounds, such as tetraphenyltin, was found in a mixture of one part by volume of concd. nitric and six parts of concd. sulfuric acids. This mixture with volatile compounds gave results that were barely acceptable, and the consistently low values indicated a loss of material.

The lesser volatility of organotin halides, their smooth oxidation to stannic oxide, and their ready formation by the addition of bromine to organotin compounds suggested a method based on a preliminary decomposition by bromine in carbon tetrachloride followed by a nitric–sulfuric acid oxidation to stannic oxide. This method has been successfully applied to a wide variety of organotin compounds and has been checked by several workers in this Laboratory. The total time required for an analysis is about six hours, but for a great part of this time (during evaporation and ignition) the analysis requires little or no attention.

Method of Analysis

About 0.5 g. sample of compound is placed in a previously weighed 60-cc. porcelain crucible.[4] The crucible is then partially immersed in an evaporating dish containing cold water.[5] A solution of bromine in carbon tetrachloride (of about 4% concentration) is added slowly with shaking.[6] Two cc. of a concd. nitric (one part) and concd. sulfuric (six parts) acid mixture is then added dropwise[7] with shaking or agitation. A reaction generally sets in with the first few drops of the acid mixture and a white precipitate forms and rises to the surface. After the first few drops of acid mixture have been added it is well to wait for a few minutes until a reaction begins. Thereafter the dropwise addition of acid is regulated by the subsidence of reaction.

In like manner there is then added 3 4 cc. of a 1:1 mixture of concd. nitric and concd. sulfuric acids. With the more volatile and reactive alkyl tin compounds it may be advisable at or prior to this point to replace the warm water in the evaporating dish by cold water. There is then added 2 cc. of concd. nitric acid and 4–5 cc. of fuming nitric acid.

The crucible is then covered by a small watch glass in a manner to permit the ready escape of fumes, and allowed to stand on a steam-plate or its equivalent for about half an hour. The contents are then heated[8] to expel the residual oxides of nitrogen and the carbon tetrachloride until a clear solution is obtained.

---

[4] Thorough shaking is difficult in a smaller-sized crucible.

[5] Such cooling is helpful in the decomposition of the more volatile compounds. Also it reduces the time required for the preliminary decomposition of all organotin compounds.

[6] The bromine should be added to a slight excess. The appearance of a brown color is not always evidence of an excess of bromine. The characteristic reddish color of bromine will appear when an excess has been added. The addition of bromine may be omitted with organotin halides of high molecular weight.

[7] The reagents are best added by keeping the tip of the pipet near the side of the crucible and above the edge of the material. During the addition, the contents of the crucible are agitated by a circular motion.

[8] This may be effected by heating in an air-bath, a convenient form of which is provided by placing a clay triangle on an evaporating dish and then heating the dish directly. Or, if time permits, the crucible may be allowed to remain on the steam-plate for a longer period than one-half hour.

The watch glass is now removed and the heat regulated until there is a slow evolution of sulfuric acid fumes. This heating is continued until all of the acid has been expelled. A grayish residue generally results. The crucible is then heated slowly by means of a small direct flame until the evolution of white fumes has practically ceased. A more intense heat is then applied, finally ending with ignition by a Méker burner. The crucible and contents are ignited to constant weight and the tin is estimated as stannic oxide.

The results of some representative analyses follow.

TABLE I

RESULTS OF ANALYSES

Compound	Sn %		
	Calcd.	Found	
Tetraethyl tin	50.53	50.66, 50.30	50.54, 50.13
Tetra-*n*-butyl tin	34.21	34.06	34.02
Tri-*n*-butyl tin bromide	32.14	32.39	32.26
Di-*n*-butyl tin dibromide	30.22	29.81	29.99
Triethyl-*p*-bromophenyl tin	32.81	32.33	32.12
Tetraphenyl tin	27.80	27.85	27.95
Triphenyl tin iodide	24.89	24.60	24.82
Triphenyl-*p*-chlorophenyl tin	25.72	25.81	25.74

The authors wish to acknowledge some check analyses carried out by C. C. Vernon and W. L. Wall.

Summary

A method has been described for the quantitative estimation of total tin in a variety of organotin compounds. The method consists of a preliminary decomposition by bromine in carbon tetrachloride followed by a nitric-sulfuric acid oxidation to stannic oxide.

AMES, IOWA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. I. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF NATURAL RUBBER

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED NOVEMBER 2, 1928 PUBLISHED APRIL 5, 1929

The destructive distillation of rubber has been studied by many investigators. Isoprene and dipentene have been isolated many times, identified and shown to be the predominating products. The existence of other products has often been detected and empirical names have been given to them. Ipatiew and Wittorf[1] have positively identified trimethylethylene; Harries[2] identified myrcene and also a terpene with a boiling point of 168–169°. Heveen (b. p. 252°) was found by Bouchardat[3]

---

[1] Ipatiew and Wittorf, *J. prakt. Chem.*, **55**, 2 (1897).

[2] Harries, *Ber.*, **35**, 3662 (1902).

[3] Bouchardat, Bull. *soc. chim.*, **24**, 108 (1875).

and Staudinger[4] recently, has isolated two compounds which he believes to be dimethylbutadiene and tetrahydrotoluene. Staudinger and associates[4,5] also state that in the distillate from destructive distillation at reduced pressure only isoprene and dipentene are present in the fraction below 200°.

The present work was undertaken largely for the purpose of throwing light upon the structural formula of the rubber hydrocarbon and, although this objective has not been attained, it is hoped that an extension of the methods of prediction developed herein to the constitution of heveen, $C_{15}H_{24}$, may eventually yield constructive results.

Procedure

Two hundred pounds of light pale crepe were destructively distilled at atmospheric pressure, in 16-lb. batches in an iron vessel connected to a suitable condensing system. No attention was paid to temperature control, due to the large size of the batches; the temperature was always raised as quickly as possible to about 700°, in order to obtain a favorable yield of isoprene, which was desired for work on synthetic rubber. The distillate is a dark-colored oil. After removal of isoprene by fractionation, the residual oil was subjected to thorough fractional distillation in a carborundum-coated spiral column.[6] Cuts were made for every degree between 50 and 176°. The customary volume of an intermediate was 5 cc., except where components were detected within 4" of each other, in which case the intermediates were larger. Several components were present to the extent of 50 cc. or more, and in such cases accurate and positive identification could be made. In other instances, 10 or 15 cc. was the maximum amount to work with. Such cases are recorded in the data only when the identification was sufficient to be certain of the series to which the component belonged.

It was later discovered that the addition of magnesium to the rubber greatly increased the yield of materials other than isoprene and dipentene. Zinc, iron and aluminum have a similar effect but to a very much smaller extent; copper is without effect; brass equals iron. A batch of 16 lb. of rubber was destructively distilled in the presence of 850 g. of magnesium and the product separately investigated. The same components were found that had been identified in the distillation of rubber alone but the proportions were different. The material from the distillation with magnesium is richer in compounds of the aromatic series and poorer in chain compounds. The liberty has been taken only in the cases of a few of the chain compounds, which were present in both cases in extremely

---

[4] Staudinger, *Helv. Chim. Acta*, 9, 549 (1920).

[5] Staudinger, *ibid.*, 9, 529 (1926).

[6] T. Midgley, *Ind. Eng. Chem.*, *20*, **April** (1929).

small quantity, of combining the same cuts in order to obtain a sufficient sample to work with.

Wherever two or more components could not be separated to purity by fractional distillation, other methods of purification were used. Distillation from aniline proved to be very useful in separating chain from hydro-aromatic compounds. Compounds of the aromatic series were treated with bromine to eliminate the ethylenic impurities and steam distilled.

Cuts were considered suitable for identification: **(1)** when the Engler distilling range was less than 2°, (2) when special tests gave positive identification of the presence of a compound in the bulk, **(3)** when the compounds present could each be identified separately and the physical properties of the mixture checked this analysis (this has been done in only one case when more than two compounds were present) or (4) when continued purification failed to alter the physical properties.

In general, physical constants were relied upon for identification. These were augmented by titration of the unsaturation with a KBr–$KBrO_3$ mixture and by determination of the molecular weight. Quantitative hydrogenation with platinum black, followed by removal of the aromatic compounds by nitration, played an important part in many identifications. Special tests were used when found in the literature. Combustion was used in cases where the C–H ratio was in doubt.

Due to the small quantity of hydrocarbon left after other methods of identification had been exhausted, the location of double bonds with potassium permanganate was rendered impracticable. Consequently, where the comparison of physical constants is not sufficiently accurate to locate a double bond or where the constants are lacking in the literature, the exact position of the double bond remains in doubt. The location is actually being determined by ozonation and will be reported later.

In addition to the components which could be separated by fractional distillation, a substantial proportion of the original material polymerized, remaining as a jelly in the distilling flask. It may be safely assumed that the materials lost in this way consisted very largely of dienes which were too unstable to distil.

Results

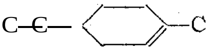
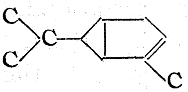
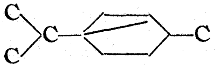
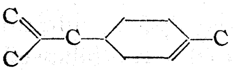
Briefly stated, the materials found were olefinic, dienic, aromatic and hydro-aromatic compounds, and a single dicyclic olefin. No fully saturated compound was detected. Table I lists the names of the compounds, the degree of accuracy of their identification and the relative quantities present in the two types of distillates.

The following paragraphs describe more completely each compound listed in the table. The common or Geneva name is used to initiate the paragraph when positive identification has been secured. It is followed by the physical constants from "International Critical Tables" (abbreviated as I. C. T.) or other sources, which are then indicated. The next listed item is the method of purification, followed by the physical constants of the purified substance. Additional data include special tests, constants of the hydrogenated compounds, special observations, etc. Where no positive identification is possible, the paragraph is headed by the word COMPONENT, followed by the physical constants found and any other data bearing on the partial identification. The boiling point ranges refer to Engler distillation from the ten-to-ninety-per cent.-over points and unless otherwise stated densities are at 20°/20° and indexes of refraction at 20°.

3-Methyl-1-Butene.—B. p., 21°; d, 0.660; n not given; mol. wt., 70. Purified by fractional distillation: b. p., 19–20°; d_{20}^{15}, 0.645; n^{18}, 1.3897; mol. wt., 66.8; double bond, 1.35. Although the material obtained was impure, there can be no doubt that the major part of it was 3-methyl-1-butene. It probably contained a low-boiling diene as impurity.

Table I

Compounds, Identification and Quantities

Compounds	Degree of identification	% in distillate Straight	 With Mg
C—C(C)—C=C	Positive	0.04	0.2
C=C(C)—C—C	Positive	.04	.2
C=C(C)—C=C	Positive	10.0	10.0
C—C(C)=C—C	Positive	.04	.2
C—C(C)=C—C—C A?	Chain structure positive	.06	.30
C—C—C(C)=C—C	Positive	.03	.15
C=C—C(C)=C—C	Positive except for position of double bonds	.03	.15
Benzene	Positive	.005	.1
C—C—C(C)=C—C—C	Chain structure positive	.03	.15
Δ^3—C—C_6H_9	Not positive	.01	.1
Δ^2—C—C_6H_9	Suspected	..	..
C—C=C—C—C—C(C)—C A?	Chain structure positive	.02	.1
Δ^1—C—C_6H_9	Positive	.1	1.0
Toluene	Positive	.05	1.0
C—C—C—C—C—C(C)=C A?	Chain structure positive	.04	.2
Dihydro-m-xylene	Positive	.1	1.0
m-Xylene	Positive	.05	1.0
 A?	Positive	.08	.8
 ?	Hydrogenation product  ?	.04	.8
p-Methylethylbenzene	Positive	.04	.8
$C_{10}H_{18}$ (1 double bond)	....	.04	.8
C—C(C)=C—C—C—C(C)=C—C Δ?	Not positive	.015	0.0
	Positive	20.0	20.0

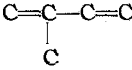
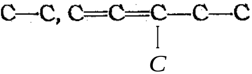
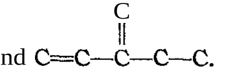
2-Methyl-1-Butene.—B. p., 32°; d_0^0, 0.667; n^{17}, 1.378. Purified by polymerization of the contained isoprene with sodium–potassium alloy, removal of the polymerized product, reduction of the remaining isoprene by sodium in liquid ammonia and subsequent fractional distillation: b. p. 30–31 °; d_{20}^{17}, 0.6645; n^{17}, 1.3752; double bond, 1.0.

Isoprene.—B. p., 34°; d, 0.679; *n*, 1.4221. Purified by fractional distillation, identified by polymerization to synthetic rubber: b. p., 33-34"; *d*, 0.671; *n*, 1.4103. Rromination indicates 1.82 double bonds per C_5H_8. Pentenes were present as impurities.

2-Methyl-2-Butene.—B. p., 38.4°; d^{13}, 0.668. Purified by fractional distillation: b. p., 36.8–38°; *d*, 0.666; *n*, 1.3927; double bonds, 1.25 per C_5H_{10}. Isoprene present as impurity.

Component 59–60°.—*d*, 0.730; *n*, 1.4117; 1.0 double bond per C_6H_{12}. Purified by fractional distillation. Hydrogenation and nitration gave a material, b. p., 60–61°; *d*, 0.654; *n*, 1.3728; mol. wt., 87. I. C. T. gives for 2-methylpentane: b. p., 60°; d, 0.654, *n*, 1.372; mol. wt., 86. These results identify the original material as a 2-methylpentene, position of the double bond unknown.

3-Methyl-2-pentene.—Isomer No. 1: b. p., 65.7"; d^{15}, 0.722; *n*, 1.4065. Isomer No. 2: b. p., 70.2°; *d*, 0.698; *n*, 1.401. Purified by fractional distillation: b. p., 62-65'; d, 0.694; *n*, 1.404; double bond, 1.07 per C_6H_{12}. Hydrogenation gave a compound b. p., 63.6–64.5°; *d*, 0.666; n, 1.3752; mol. wt., 86. I. C. T. gives for 3-methylpentane: b. p., 64°; *d*, 0.668, *n*, 1.377, mol. wt., 86.

Component 76–79°.—Purified by aniline fractionation: *d*, 0.742; n, 1.4346; double bonds, 1.58 per C_6H_{10}. Partially hydrogenated, then extracted with H_2SO_4; adding water to the acid liberates an oil which gave on redistillation: b. p. 67–68°; *d*, 0.712; *n*, 1.4060; mol. wt., 83. Bromine reacted slowly. I. C. T. gives for 3-methyl-2-pentene two isomeric forms of which the average is: b. p., 67.8"; d, 0.712; *n*, 1.4039; mol. wt., 84. The following deductions may be made: 1.58 double bonds shows the presence of a diene in the original material; the partial hydrogenation and the extraction show that the carbon structure of this diene corresponds to 3-methyl-pentadiene. The forms compatible with the experimental results are:  $C{=}\underset{\substack{|\\C}}{C}{-}C{=}C{-}C$,  $C{=}C{=}\underset{\substack{|\\C}}{C}{-}C{-}C$ and  $C{=}C{-}\overset{\substack{C\\\|}}{C}{-}C{-}C$. The only diene given in the literature boiling at 76–79' is 3-methyl-1,3-pentadiene, for which the constants by Abelmann are: b. p., 76–79"; d_4^0, 0.7576, $n^{16\ 5}$, 1.45427. *A* mixture of 64% of this diene, 31% of 3-methyl-2-pentene and 5% benzene will yield physical constants in close agreement with those of the original mixture. 3-Methyl-2-pentene and benzene are the adjoining and identified components. The identification is not considered as positive, despite the strong evidence.

Benzene.—M. p., 5.6"; b. p., 79.6"; *d*, 0.878; *n*, 1.5014.—Purified by aniline fractionation followed by a treatment with bromine and distillation: 2 cc. of purified material was obtained; m. p., +2°; n, 1.4995; characteristic odor of benzene.

Component 93-G°.—Purified by fractional distillation: d, 0.744, *n*, 1.422; 1.06 double bond per C_7H_{14}. Hydrogenation and nitration gave a compound: b. p., 92–95"; d, 0.723; *n*, 1.4032, which contained hexahydrotoluene as an impurity. The physical constants are not in sufficient agreement with anything in the literature to allow a possible identification. The nearest physical constants given are for d-3-methylhexane: b. p., 92°; d, 0.687. The physical constants of the hydrogenated product show that it contained a large proportion of a paraffinic hexane, the boiling point of which corresponds to the one given for 3-methylhexane. Identification considered incomplete.

Δ^3-Tetrahydrotoluene.—B. p., 103°; *d*, 0.799; n, 1.443. Purified by fractional distillation: b. p., 102–103°; d, 0.791; *n*, 1.444; double bond, 1.08 per C_7H_{12}. Hydrogenation gave a compound, b. p., 100–102°; *d*, 0.7671; n, 1.4225. I. C. T. gives for methylcyclohexane: b. p., 100.8°; *d,* 0.764; n, 1.4235. Nitration failed to detect aromatic compounds.

A²-Tetrahydrotoluene.—Not purified enough for identification; a sufficient intermediate persisted in the general distillation to suggest its presence.

Component **109–110°.—Purified** by aniline fractionation: d, 0.783; *n,* 1.4413; double bond, 1.13 per C_7H_{14}. Hydrogenation and nitration indicated toluene as an impurity. Further purification of the saturated compound by fractional distillation gave a small quantity of hexahydrotoluene and of iso-octane: b. p., 116"; d, 0.706; *n,* 1.397. I. C. T. gives for iso-octane: b. p., 116°; d_4^{15}, 0.704; *n,* 1.3964.

Δ¹-Tetrahydrotoluene.—B. p., 111°; *d,* 0.809; *n,* 1.4496. Purified by fractional distillation: b. p., 110–111°, d, 0.818; *n,* 1.4653. Special test (Beilstein): 3 drops of sulfuric acid added to an alcoholic solution of the hydrocarbon gave a green coior peculiar to A¹-tetrahydrotoluene. Double bonds, 0.75, indicating a large percentage of toluene. Hydrogenation and nitration yielded a large quantity of trinitrotoluene and hexahydrotoluene: b. p., 100°; *d,* 0.762; *n,* 1,423. I. *C.* T. gives for hexahydrotoluene: b. p., 100.8"; *d,* 0.764; *n,* 1.4235.

Toluene.—B. p., 110.5"; *d,* 0.866; *n,* 1.4962. Purified by aniline fractionation, treatment with bromine and steam distillation: b. p., 110° sharp; identified by its odor and nitration to mononitrotoluene, b. p., 220°, the latter also having a characteristic odor.

Component 121–122°.—*d,* 0.765; n, 1.4287; hydrogenation and nitration indicated the presence of a small amount of aromatic compounds and gave a material: b. p., 116–121°; d, 0.739; n, 1.4102; mol. wt., 112.4, indicating iso-octane with a small quantity of hexahydro-m-xylene as an impurity. A fraction 124–125" gave a hydrogenation product with a slightly higher boiling range, density and index of refraction, indicating another isomeric form of 2-methylheptene containing an increased quantity of hexahydro-m-xylene. Although the above two fractions were present in the distillation in sufficient quantity to indicate the presence of components, there was not enough for proper purification and identification; all indications were that they were isomeric methylheptenes, probably 2-methylheptenes, with the location of the double bond totally unknown.

Dihydro-m-xylene, Probably **Δ-1,3.**—No constants given in the literature. Purified by aniline fractionation: b. p., 129–130°; *d,* 0.795; n, 1.4451. Hydrogenation and nitration indicated the presence of a small quantity of xylene and of a compound, b. p., 122–129°, bulk at 125°; *d,* 0.764; n, 1.4208; mol. wt., 112.6. I. C. T. gives for hexahydro-m-xylene: b. p., 123.7'; *d,* 0.771; *n,* 1.425; mol. wt., 112. These properties identify hexahydro-m-xylene with a small amount of paraffinic compounds as impurity. **A** substantial part of the original cut obtained by fractional distillation containing the dihydro-m-xylene was treated with bromine; no dibromides were found, only tetrabromides.

***m*-Xylene.**—B. p., 139°; *d,* 0.865; n, 1.4973.—Purified by treating with an excess of bromine water, and steam distilling; redistilling several times to eliminate all traces of bromides gave a material, b. p., 137°; *d,* 0.866. Nitration to the trinitro compound gave white crystals melting sharply at 179.5°. **Mulliken** gives m. p. 180–181° for trinitro-m-xylene. It is thus shown that the xylene obtained was pure m-xylene containing no trace of either ortho or para derivatives.

***p*-Tetrahydro-Ethyltoluene.**—Beilstein gives for the Δ³-compound: b. p., 149°; d, 0.816; n^{16}, 1.453. Purified by fractional distillation: b. p., 144–145°; *d,* 0.813; *n,* 1.4529; double bond, 1.2 per C_9H_{16}. Hydrogenation and nitration gave a material: b. p., 147°; *d,* 0.784; *n,* 1.4335; mol. wt., 123. Beilstein gives for *p*-hexahydro-ethyltoluene: b. p., 147°; d_4^{15}, 0.788; n^{15}, 1.435; mol. wt., 126. There can be no question of the identification except for the position of the double bond, which may have been Δ^1 instead of A^3; no physical constants are available for the Δ^1-compound.

Component **158–159°.**—*d*, 0.834; *n*, 1.4665; double bond, 0.998. Purified by fractional distillation; composition by combustion, $C_{10}H_{16}$, establishing the presence of a dicyclic compound. I. C. T. gives for thujene: b. p., 151°; d, 0.830; *n*, 1.4515. Hydrogenation and nitration gave a material, b. p., 158–161°; *d*, 0.813; *n*, 1.4498; mol. wt., 133.5–134.8 (theoretical for $C_{10}H_{18}$, 138); double bond, 0. Combustion gave $C_{10}H_{18}$ within 0.2%. Beilstein gives for thujane: b. p., 157°; d, 0.814–0.819; *n*, 1.4376-1.44395. Off-hand it would appear that the identification of the original material, as an isomeric form of thujene, was as definite as many of the foregoing identifications, but more careful consideration indicates that such is not the case. Identification by physical constants requires not only that the physical constants of the unknown be in close agreement with those of likely possibility, but that all, or nearly all, of the possibilities be known and listed, and that the constants are not in agreement with any of the other possibilities. This has been the case with all the components positively identified in C_5, C_6, C_7, C_8 and C_9, but it is not so with the dicyclic compound in C_{10}. It was therefore decided to consider the identification of this component as unestablished.

***p*-Ethyltoluene.**—B. p., 162; d, 0.862; *n*, 1.4943. Purified by treating with bromine water and steam distilling: b. p., 160.5–163°; *d*, 0.866; n, 1.4832; mol. wt., 120.4, instead of 120, theoretical; saturated toward bromine; oxidation with permanganate yields terephthalic acid.

Component 162–163°.—*d*, 0.828; *n*, 1.46; mol. wt. 130.5; bromination indicated 1.0 double bond. Obtained only from rubber decomposed in the presence of magnesium. Hydrogenation and nitration gave a compound b. p., 162–164°; *d*, 0.794; n, 1.4407; saturated toward bromine; mol. wt., 135; combustion indicated a formula of $C_{10}H_{20}$ within 0.2%. This shows that the original material was of empirical formula $C_{10}H_{18}$. The hydrogenation was a quantitative check on the original bromination. It is evident that this is a single ring compound containing 1 double bond. It is impossible to identify this compound from any known data.

Component **162–163°.**—The distillate from rubber alone gave a component in this boiling range: d, 0.8105; *n*, 1.456; double bond, 1.4. Aniline fractionation failed to purify it further. Thus it is seen that the distillation of rubber alone gives a lighter material than the distillation with magnesium and that the unsaturation is 1.4 instead of 1.0 double bond, indicating the presence of a dienic compound. If this density be extrapolated to 100% diene, 0.783 is obtained. By a separate synthesis,[7] a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes was obtained, the physical constants of which were: b. p., 163–164°; d, 0.773. Considered as not a positive identification, but as strong evidence that a dimethyloctadiene was present.

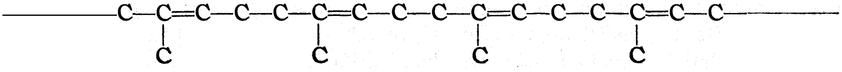
Dipentene.—B. p., 176°; d^{18}, 0.865; *n*, 1.471. The density given by I. C. T. is apparently an error; Schimmel and Company give 0.844; Brühl gives $d_4^{20.85}$, 0.8402; Staudinger, d^{20}, 0.841. Purified by fractional distillation: b. p., 176°; *d*, 0.8435; *n*, 1.4712; double bonds, 1.96. Hydrogenation gave p-menthane: b. p., 170–171.2'; *d*, 0.796; n, 1.4387. I. C. T. gives for p-menthane: b. p., 170°; d, 0.793; *n*, 1.437. No evidence was obtained of the presence of myrcene, or a terpene, b. p., 168–169°, or of dimethylbutadiene.[4]

Derivation of the Structural Formula of the Products from That of Rubber.—Prior to entering upon this investigation, a method had been developed for illustrating the mechanism by which isoprene and dipentene form during destructive distillation. After the above results were ob-

---

[7] Midgley and Henne, THIS JOURNAL, 51, 1294 (1929).

tained, it was felt that the method should be extended to include as many of the products as possible. A relatively simple solution is herewith presented which completely covers a majority of the cases, a few partially, and leaves only the formation of benzene without explanation. The long-chain structural formula for rubber hydrocarbon[8] is broken at single



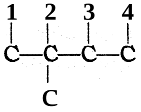
$$—C-\underset{\underset{C}{|}}{C}=C-C-C-\underset{\underset{C}{|}}{C}=C-C-C-\underset{\underset{C}{|}}{C}=C-C-C-\underset{\underset{C}{|}}{C}=C-C—$$

Staudinger formula for rubber

valences to give a section containing a given number of carbon atoms. The points of breakage are represented by partial valences and the double bonds are resolved into partial valence form. This is called the transient *form*. The following postulates are then observed: (1) adjacent partial valences may join to form double bonds (Thiele); (2) single partial valences six carbons apart may join to form rings; (3) any pair of partial valences may accept hydrogen, preferably those not adjacent to others; (4) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic compounds; (5) partial valences not joining nor accepting hydrogen may migrate.

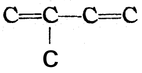
After having derived all of the combinations by applying the above assumptions to a transient form, the resulting stable forms are examined and those forms cast out which experimental data show do not form by pyrolytic decomposition. Predominant among these are molecules containing a carbon atom in a ring bonded to two other carbon atoms external from the ring and those containing a methylene group attached to a ring. The formation of dienic compounds has been disregarded, since no experimental data were obtained.

The mechanism of the reactions involving 5 carbon atoms (called compounds in C_5 for simplicity) may be represented as follows



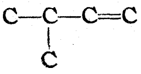
$$\overset{1}{\overset{|}{C}}-\underset{\underset{C}{|}}{\overset{2}{\overset{|}{C}}}-\overset{3}{\overset{|}{C}}-\overset{4}{\overset{|}{C}}$$

Transient form in C_5



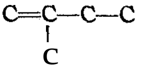
$$C=\underset{\underset{C}{|}}{C}-C=C$$

Isoprene



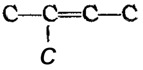
$$C-\underset{\underset{C}{|}}{C}-C=C$$

3-Methyl-1-butene



$$C=\underset{\underset{C}{|}}{C}-C-C$$

2-Methyl-1-butene



$$C-\underset{\underset{C}{|}}{C}=C-C$$

2-Methyl-2-butene

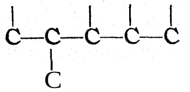
Because of the preponderance of isoprene(C_5), dipentene(C_{10}) and heveen(C_{15}) in the products of destructive distillation, it is held certain that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis. The same conclusion is arrived at by C. D.

---

[8] Staudinger, *Ber.*, 44, 2212 (1911); 46, 2466 (1913); *Helv. Chim. Acta,* 5, 743 (1922); 5, 756 (1922); 5, 785 (1922); *Ber.*, 57, 1203 (1924); *Helv. Chim. Acta,* 7, 842 (1924); *Z. angew. Chem.,* 38, 226 (1926).

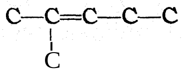
Hurd, starting from purely theoretical considerations,[9] and is found to hold when the other pyrolysis products of rubber are examined. Hence the transient form shown above predominates in C_5 to the practical exclusion of the two other possible forms. Four stable forms are derived from it: isoprene by the joining of 1 with 2 and 3 with 4, 3-methyl-1-butene by the acceptance of hydrogen on 1 and 2 and the joining of 3 with 4 and 2-methyl-1-butene by the acceptance of hydrogen on 1 and 4 and the joining of 2 with 3. Isoprene predominates, since it requires no hydrogen to produce a stable form.

In C_6, two transient forms are possible. Each case requires that a bond adjacent to a double bond be broken. The proportion of C_6 compounds should therefore be small. In neither case does a stable form result without either migration or hydrogen acceptance.



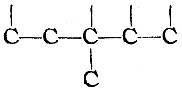
$$\overset{|}{C}-\underset{\underset{C}{|}}{C}-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

Transient form No. 1 in C_6



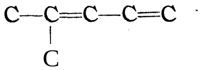
$$C-\underset{\underset{C}{|}}{C}=C-C-C$$

2-Methyl-2-pentene



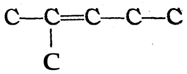
$$\overset{|}{C}-C-\underset{\underset{C}{|}}{\overset{|}{C}}-\overset{|}{C}-\overset{|}{C}$$

Transient form
No. 2 in C_6



$$C-\underset{\underset{C}{|}}{C}=C-C=C$$

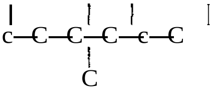
3-Methyl-1,3-pentadiene



$$C-\underset{\underset{C}{|}}{C}=C-C-C$$

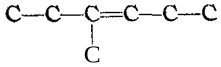
3-Methyl-2-pentene

There is only one transient form possible in C_7. It requires the breaking of two single bonds adjacent to double bonds. It is obvious that valences 1 and 6 may either accept hydrogen to form 3-methyl-3-hexene or join to form Δ^1-tetrahydrotoluene, the dehydrogenation of which gives toluene.



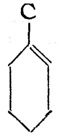
$$\overset{|}{C}-C-\underset{\underset{C}{|}}{\overset{|}{C}}-\overset{|}{C}-C-\overset{|}{C}$$

Transient
form in C_7



$$C-C-\underset{\underset{C}{|}}{C}=C-C-C$$

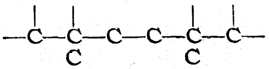
3-Methyl-3-hexene



Δ^1-Tetrahydrotoluene

Toluene

C_8 exhibits the possibility of only one transient form and in a similar manner to C_7 partial valences 1 and 6 may either hydrogenate to form a dienic compound or join to form dihydro-m-xylene, the dehydrogenation of which gives m-xylene.



$$-\overset{|}{C}-\underset{C}{\overset{|}{C}}-C-C-\underset{C}{\overset{|}{C}}-\overset{|}{C}-$$

Transient form in C_8

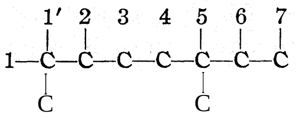
Dihydro-*m*-xylene

m-Xylene

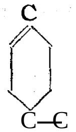
---

[9] C. D. Hurd, "The Pyrolysis of Carbon Compounds," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1929.

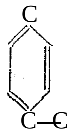
C_9 again presents two possible transient forms. The only evidence obtained covering the many possibilities in C_9 was in connection with transient form 1, which appeared to accept hydrogen by 1 and 1′, 2 joining with 7 and 5 with 6. The dehydrogenation of the resulting tetrahydro-*p*-ethyltoluene yields p-ethyltoluene. Other ring forms suggested as possible products of transient form 1 or 2 could not be detected.



Transient form
No. 1 in C_9

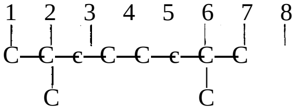


Tetrahydro-*p*-
ethyltoluene

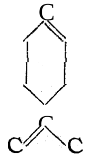


p-Ethyltoluene

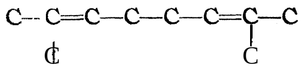
In C_{10}, as in C_5, three transient forms are possible, but since one of them is obtained by the rupture of only weak bonds, it should be predominant; it stabilizes without migration or hydrogenation by the joining of 3 with 8, 1 with 2 and 6 with 7, giving dipentene. By accepting hydrogen in 1,8 it stabilizes to dimethyloctadiene.



Predominating
transient form in C_{10}

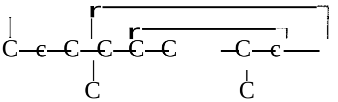


Dipentene

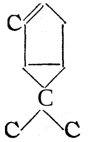


Dimethyloctadiene

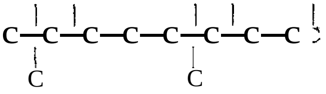
The other transient forms present an interesting speculation in connection with the component 158–159° (shown to be a dicyclic compound $C_{10}H_{16}$), and component 162–163° (shown to be a single ring compound $C_{10}H_{18}$). The development from transient form 2 serves as a suggestion of the mechanism of the formation of a dicyclic compound, while the development from transient form 3 is a suggestion, predicated on the behavior of form 1 in C_9, to show the acceptance of hydrogen and subsequent ring formation. Both derivations are only speculations. If these suggestions could be proved experimentally, an interesting generality might be derived, namely, that when a terminal carbon atom has two partial valences attached to it, dicyclic ring formation is favored, but when an internal carbon is in the same case, hydrogen acceptance is favored,



Transient form
No. 2 in C_{10}



Isomeric
thujene



Transient form
No. 3 in C_{10}

Component
162°?

The identification of A^3-tetrahydrotoluene and the evidence for the existence of A^2-tetrahydrotoluene among the products is not predictable. It is felt, however, that migration of the double bond from the Δ^1-position should not be considered as unlikely, since the amounts of Δ^2- and Δ^3-compounds were exceedingly small.

Discussion

In view of the evidence at hand, it can scarcely be doubted that with the exception of benzene the compounds of the aromatic series present were all derived by dehydrogenation of the corresponding hydro-aromatic forms, since only those aromatic compounds are found whose hydro-derivatives are also present. Dihydro-m-xylene is the only predictable ring compound in C_8, hence if dehydrogenation occurs, only m-xylene should result. If, on the other hand, m-xylene is a primary pyrolysis product, small amounts of the ortho and para derivatives at least should be present. Particular care was taken to ascertain that no other xylene was present than the meta derivative. The same reasoning holds true in C_9 with respect to pethyltoluene. A reason for the dehydrogenation during destructive distillation is not apparent. It is well known that cyclohexane in the presence of nickel and at similar temperatures will dehydrogenate to benzene, but there was no catalyst present to account for a similar behavior during pyrolysis of rubber alone. It is significant that the presence of magnesium in the rubber increases decidedly the proportion of aromatic compounds.

The origin of benzene is obscure. It is not due to accidental contamination in the laboratory, since the presence of a metal in the rubber always increases the amount of benzene in the distillate. Extreme pyrolysis in locally overheated spots might account for its formation.

To sum up, of the **23** compounds identified, 12 were in perfect agreement with the postulated results, 5 were in agreement as far as their identification was possible and rational explanations of the other 6 are not at variance with the postulates. In C_5 all forms predicted were obtained, in C_6, C_7 and C_8 chain compounds only were missing from the predictions. In C_9 the only logical rings were obtained, in fact, and in C_{10} all normal predictions were fulfilled.

Relationship of the Results to the Structural Formula of Rubber.—The constitution of the ten-carbon section of rubber has been thoroughly established by oxidation and confirmed by many investigators, but assemblage of these units into the complete structural formula of rubber has been the basis of much work and argument. Harries originally interpreted the results of his oxidations as indicating the existence of an eight-sided ring. He was more or less driven from his original interpretation in later years. Staudinger and co-workers[4,8] support fa long-chain structure in which the ten carbon atom sections recur and are bonded together by ordinary valences, thus requiring no residual valences to account for the structure. Many intermediate speculations have been indulged in.

The results of this investigation throw no additional light upon the discussion. The use of the long-chain formula affords greater ease for interpretation, but the results do not contradict Harries viewpoint. Recently, E. A. Hauser[10] has supported the hypothesis that the rubber molecule is a long chain arranged in helix form, by interpreting the x-ray pattern of stretched rubber. The predominant formation of six-sided rings in C_7, C_8, C_9 and C_{10} appears to support this hypothesis, since to account for ring formation upon any other arrangement that has been advanced requires the joining of partial valences across the space occupied by six carbon atoms, whereas a helix may be so arranged that the carbon atoms, six apart in the chain, may be adjacent in space.

Conclusions

All of the products of the destructive distillation of natural rubber are directly derived, by simple reactions, from the rubber molecule. Those compounds predominate which represent sections of the rubber molecule occurring between the single bonds furthest removed from the double bonds.

Summary

Two hundred pounds of pale crepe rubber have been destructively distilled at atmospheric pressure. The distillate was fractionated and its components identified from C_5 to C_{10}, as shown in the table. Assuming that the Staudiiger formula is correct, that the single bonds furthest from the double bonds are the weaker spots and that the formation of six-carbon rings is favored, it has been shown that nearly all of the compounds actually isolated could be predicted. The experimental results, together with forthcoming experimental data, are expected to be used to throw light upon the formula of the rubber molecule.

ITHACA, N. Y.

---

[10] E. A. Hauser, address at the Swampscott Meeting of the American Chemical Society, September, 1928.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF THE GRIGNARD REAGENT ON HIGHLY BRANCHED CARBONYL COMPOUNDS[1]

BY J. B. CONANT[2] AND A. H. BLATT[3]

RECEIVED NOVEMBER 3, 1928 PUBLISHED APRIL 5, 1929

While a great variety of straight-chain aliphatic compounds of large molecular weight are known, the information in regard to many groups of branched aliphatic compounds is relatively meager. For example, of the 38 tertiary alcohols listed in the new edition of Beilstein's "Handbuch" (which covers the literature to 1910), 32 contain only primary alkyl groups. Of the remaining 6, four contain one secondary group and two primary groups, while only two contain a tertiary group; none contains more than one secondary or tertiary group. Although a great deal of work in aliphatic chemistry has been published in the last eighteen years, our information concerning branched compounds has not materially increased. Purely aliphatic carbinols of the type[4] $(R^3)_3COH$, $(R^2)_2R^3$-COH and $(R^2)_3COH$ appear to be still unknown.[5] In regard to the hydrocarbons our information is even more restricted. The only hexa-alkylethanes, $(R_3C–CR_3)$, that have been prepared are hexamethylethane[6] and tetramethyldiethylethane.[7] Hexa-alkylethanes containing branched alkyl groups are entirely unknown.

The facts which are available regarding branched aliphatic compounds indicate that these compounds possess highly interesting properties, and indicate further that predictions as to the behavior of branched compounds based on the behavior of their primary straight-chain analogs are likely to be quite misleading. For example, the reaction of *iso*propyl alcohol with the halogen acids to form the isopropyl halides is often given as a typical reaction of secondary alcohols. Now there are six

---

[1] This paper contains results obtained in an investigation on "Isolation and Investigation of Thermo-Labile Hydrocarbons Present in Petroleum," listed as Project 16 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project 16.

[3] American Petroleum Institute Research Fellow.

[4] We shall use R^1, R^2 and R^3 to represent primary, secondary and tertiary groups, respectively.

[5] A few alicyclic compounds are known of the type $(R^2)_3COH$; thus Murat and Amouroux, Bull. *soc. chim.*, [4] **15**, 159 (1914) prepared di-*iso*propylcyclohexylcarbinol, while Zelinsky, Ber., **60**, 713 (1927), has recently prepared tri-cyclohexylcarbinol.

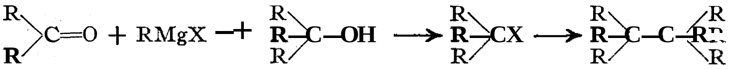
[6] Richards, Ann. *chim. phys.*, **21**, 323 (1910); Henry, Bull. *acad. roy. belg.*, **1906**, *256, 352; Compt. rend.*, **142**, 1075 (1906).

[7] Späth, *Monatsh.*, *34*, 1982 (1913).

different classes of secondary alcohols possible, according to whether the alkyl groups are primary, secondary or tertiary and alike or different. Examples of each of these classes are known. With members of five of these classes the behavior when treated with halogen acids has been studied and for only one class, that where both alkyl groups are primary is the behavior similar to that of *iso*propyl alcohol. The members of the other classes yield halides formed as a result of rearrangement, or yield oxonium salts and no halides.

In still another respect do branched alkyl groups differ from straight-chain groups, for recent work has shown that with the tetra-aryldialkylethanes[8] and the dialkyldixanthyls,[9] secondary alkyl groups are markedly more effective than primary in promoting the dissociation of carbon–carbon linkages.

Since the information regarding highly-branched aliphatic compounds, in particular tertiary alcohols and hexa-alkylethanes, is thus extremely meager, we have attempted to prepare complex tertiary alcohols and from them hexa-alkylethanes by the following general procedure



The peculiarities of highly-branched compounds became apparent earlier than expected and blocked the project at the first step. It was found that the typical addition reaction between ketones and the Grignard reagent ceases to be the main reaction as soon as highly-branched compounds are employed. We have studied a variety of branched compounds in this reaction and from our results and the data available in the literature it is possible to state the limits of usefulness of the Grignard reaction as a method of preparing secondary and tertiary alcohols (employing the procedures now available).

Besides the normal addition of Grignard reagents to carbonyl compounds three other important reactions have been noted. These are reduction, enolization and condensation. Which of these four reactions will predominate in a given case depends largely on the nature of the alkyl groups present in the Grignard reagent and in the carbonyl compound. When primary alkyl groups are present the addition reaction appears to prevail to such an extent that satisfactory yields of the desired carbinols may always be expected. Complications arise, however, when branched alkyl groups are present in the carbonyl compound or the reagent or in both. The following table gives a general summary of the phenomena. In it the letters A, R, E and C refer, respectively, to addition, reduction,

---

[8] Conant and Bigelow, This Journal, 50,2041 (1928); Ziegler and Schnell, Ann., 437,237 (1924).

[9] Conant, Small and Sloan, *ibid.*, 48,1743 (1926).

enolization and condensation. Yields are not given in exact figures because the results, taken from data of several workers, are not strictly comparable, but an approximate idea of the extent of the reaction is denoted by doubling the letter for yields greater than 50%.

Table I

Summary of Results

	CH_3MgI	*n*-C_3H_7MgBr or *n*-C_4H_9MgBr	$(CH_3)_2CHMgBr$	$(CH_3)_3CMgCl$
CH_3CHO	AA[a]	....	A[b]	AA[c]
$(CH_3)_2CHCHO$	A"	....	AA	AR
$(CH_3)_3CCHO$	..	*n*-C_3H_7MgBr AA[d]	AR[d]	RR[d]
CH_3COCH_3	AA"	....	AA"	A[f]
$C_2H_5COC_2H_5$	AA[g]	*n*-C_4H_9MgBr AA	AA[g]	C
$CH_3COCH(CH_3)_2$	AA[g]	....	AA (R)[g]	...
$CH_3COC(CH_3)_3$	AA[f]	*n*-C_4H_9MgBr AR	EC	EC
$(CH_3)_2CHCOCH(CH_3)_2$	AA[g]	*n*-C_4H_9MgBr	RK	RR
$(CH_3)_2CHCOC(CH_3)_3$	AA	....	RR	RK
$(CH_3)_3CCOC(CH_3)_3$	AA	(No reaction with C_6H_5MgBr)	R	RR
$(CH_3)_2CHCO_2C_2H_5$	...	....	RR[g]	...
$(CH_3)_3CCO_2C_2H_5$	...	....	...	No reaction
$C_6H_5CH_2CO_2C_2H_5$	...	....	EE, *CC*	...

[a] Grignard, Ann. *chim. phys.*, [7] *24*, 464 (1901).

[b] Pickard and Kenyon, *J. Chem. Soc.*, *101*, 628 (1912).

[c] **All** facts given in this table and elsewhere in this article for which no reference is given are based on the experimental part of this work.

[d] Conant, Webb and Mendum, This journal, 51, 1246 (1929).

[e] Ziegler, Ann., 437, 244 (1924).

[f] Henry, *Bull. ncad. roy. belg.*, **352** (1906).

[g] Stas, *Bull. soc. chim. belg.*, 35, *379* (1926).

The first and most striking fact shown by this table is that it has not been possible to prepare tertiary alcohols containing more than two secondary or tertiary groups. For when the simplest ketone containing two secondary groups, isobutyrone, is treated with the reagent from isopropyl bromide or *tert.*-butyl chloride the product, formed in an 80% yield, is di-isopropylcarbinol. There is no evidence of addition. When isopropyl *tert.*-butyl ketone or di-*tert.*-butyl ketone is treated with these same reagents reduction again occurs, the corresponding secondary alcohols being formed. Even in the case of aldehydes the reduction reaction is very evident when a secondary Grignard reagent acts on trimethylacetaldehyde and no addition occurs when *tert.*-butylmagnesium chloride is employed.

The special behavior of the methyl and benzyl reagents, a fact not shown in Table I, should be emphasized. Thus with isobutyrone and methylmagnesium iodide, addition to the extent of 78% takes place. In the course of some other work we found that this same ketone will add benzylmagnesium chloride, giving an 80% yield of tertiary alcohol. If now isobutyrone is treated with ethylmagnesium bromide[10] the yield of tertiary alcohol drops to 54% and is accompanied by 23% of reduction; with n-propylmagnesium bromide there is 30% of addition and 30% of reduction, while butylmagnesium bromide gives 40% of addition and 13% of reduction.

If we attempt to correlate structure and amount of reduction the facts of the preceding paragraph give a first clue that for a given carbonyl compound the amount of reduction increases with the size of the alkyl groups in the reagent. This same effect is also shown by pinacolone. With methylmagnesium iodide,[11] there is no reduction; with propylmagnesium chloride[12] there is 20% of reduction, and with butylmagnesium bromide over 30% of reduction. Much more important than the size of the alkyl group in the reagent is its complexity. The reduction of isobutyrone by n-butylmagnesium bromide amounts to 13%; with *tert.*-butylmagnesium chloride there is 80% reduction and no evidence of addition.

Just as an increase in the size and complexity of the alkyl group in the reagent promotes reduction, so also does an increase in the size and complexity of the alkyl groups in the carbonyl compound. Leroide[13] showed that while ethyl isobutyrate on treatment with n-propylmagnesium bromide gave a tertiary alcohol, ethyl pelargonate with the same reagent yielded a secondary alcohol. The effect of branching the carbon chain is shown by the behavior of diethyl ketone, isobutyrone and pinacolone toward n-butylmagnesium bromide. With the first ketone addition only is observed, with the second there is 13% of reduction and with the third 30% of reduction.

This effect of branching the alkyl groups in the carbonyl compound and reagent limits the usefulness of the Grignard reaction in preparing tertiary alcohols but it furnishes a convenient method for the reduction of highly branched ketones to the corresponding secondary alcohols. Thus isobutyrone, pentamethyl acetone and hexamethyl acetone are reduced by *tert.*-butylmagnesium chloride with excellent yields; the reduction is easily carried out and should be of use in working with branched compounds.

Besides reduction we have also encountered enolization and condensation. These two reactions seem to be limited to methyl ketones or to carbonyl compounds with a CH_2 group adjacent to the functional group, for they were encountered only with pinacolone and diethyl ketone.

---

[10] Stas, *Bull. soc. chim. belg.*, 35,379 (1926).

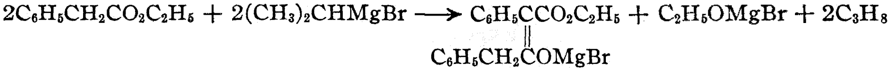
[11] Henry, *Bull. acad. roy. belg.*, 352, (1906).

[12] Leroide, *Ann. chim. phys.*, [9] 16,361 (1921).

[13] Leroide, ref. 12, p. 354.

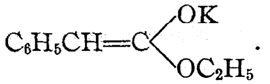
Our evidence for enolization was the recovery of the ketone from reactions where an excess of the reagent was present, coupled with the known enolizing effect of the Grignard reagent which has recently been pointed out by Grignard[14] and by Kohler.[15] By condensation in the above cases we refer to the formation of material of high boiling point.

Our most striking illustration of enolization and condensation is furnished by phenylacetic ester. When this ester is added to *iso*propylmagnesium bromide there is a steady evolution of gas (a saturated hydrocarbon) and on decomposing the reaction mixture the product is α,γ-diphenylacetoacetic ester, the acetoacetic ester condensation product of the original ester; the yield is over 90%.



$$2C_6H_5CH_2CO_2C_2H_5 + 2(CH_3)_2CHMgBr \longrightarrow C_6H_5\underset{\overset{\|}{C_6H_5CH_2COMgBr}}{C}CO_2C_2H_5 + C_2H_5OMgBr + 2C_3H_8$$

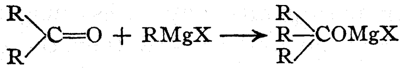
This condensation, effected only with difficulty by using dry sodium ethylate,[16] can also be carried out using metallic potassium and in this case Scheibler[17] has advanced evidence to show that the intermediate product is



$$C_6H_5CH{=}C\Big\langle\begin{matrix}OK\\OC_2H_5\end{matrix}.$$

One more Grignard reaction may be mentioned as illustrating the limiting case of the effect of branched alkyl groups. When ethyl trimethylacetate was treated with *tert.*-butylmagnesium chloride no reaction could be observed even after boiling the reaction mixture for ten hours; the ester was recovered unattacked.

Any discussion of the mechanism of these abnormal reactions must be at present largely a restatement of the experimental facts. The following seems to be the most satisfactory. With simple, straight-chain compounds the normal addition reaction takes place very rapidly



$$\begin{matrix}R\\R\end{matrix}\Big\rangle C{=}O + RMgX \longrightarrow \begin{matrix}R\\R\\R\end{matrix}\Big\rangle COMgX$$

As the alkyl groups present are increased in size and complexity, there is a decrease in the rate of this addition reaction. This would be expected in view of the known effect on the rate of bisulfite addition to carbonyl compounds of increasing the size and complexity of the alkyl groups in these compounds. When the normal addition reaction is slowed down sufficiently, other reactions, ordinarily too slow to be observed, and which are less subject to hindrance, become predominant. This is illustrated by the reduction of isobutyrone, pentamethyl acetone and hexamethyl

---

[14] Grignard and Savard, (a) *Compt. rend.*, 179, 1573 (1924); (b) *Bull. soc. chim. belg.*, 36, 97 (1927).

[15] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

[16] (a) Newbauer, "Dissertation," Leipzig, 1889; (b) Volhard, *Ann.*, 296, 1 (1897).

[17] Scheibler and Mahboub, *Ber.*, 60, 564 (1927).

acetone and by the enolization and condensation of pinacolone when branched reagents are used. The limiting case, when all reactions are slowed down to such an extent as to be negligible in rate, is that of trimethylacetic ester and ter!?.-butylmagnesium chloride where no reaction takes place. When the hindrance to addition is great but reduction and enolization are not possible because of the structure of the ketone and reagent, there is no reaction; this is the case with phenylmagnesium bromide and hexamethyl acetone. The assumption that the rate of the enolization and reduction reactions is less affected than the addition reaction by what we may call steric factors is in accord with many rate measurements on a variety of organic reactions.

Experimental

Since essentially the same procedure was employed in all the Grignard reactions it will be economical of space to give here a general description of this procedure; then in the individual cases any variations used will be noted. The reagent was prepared in the usual apparatus, a flask fitted with a trident adapter in which were placed a condenser, dropping funnel and mercury-seal stirrer. Five hundred cc. of ether was used per mole of alkyl halide and magnesium. The average yields with the various reagents were as follows: n-butylmagnesium bromide, 80%; isopropylmagnesium bromide, 70–75%; *tert.*-butylmagnesium chloride, 50–55%. In preparing *tert.*-butylmagnesium chloride a solution of 5 cc. of *tert.*-butyl chloride and 50 cc. of ether was added to the magnesium plus a crystal of iodine. After the reaction had started (two or three minutes) an additional 75 cc. of ether was added at once and then the remainder of the ether and alkyl halide mixed and added slowly. After the reagents had been prepared they were chilled, then decanted into a second flask in order to separate any excess magnesium. The second flask was surrounded by an ice-bath and then the carbonyl compound, dissolved in dry ether, was added slowly. The ice-bath was removed, the mixture stirred at room temperature for several hours or left overnight and then boiled for one hour. Finally it was cooled, decomposed with ice and a bare excess of sulfuric acid[18] and the ether layer separated. The aqueous layer was extracted once with ether and the combined ether layers washed with water, sodium carbonate solution and water and then dried over sodium sulfate. The final working up of the products varied, of course, according to their properties. The practical distillations were carried out using a Widmer special column which was found very efficient.

The reagents in general were not analyzed, but knowing the yields to be expected, a large excess of the reagent was used. In the one case,

---

[18] If hydrochloric acid is used for the decomposition there is danger, with *tert.*-alcohols, of forming the ether-soluble chlorides.

tert.-butylmagnesium chloride, where the yield of reagent may vary within wide limits it is, fortunately, quite easy to detect poor preparations, for the magnesium chloride etherate formed in such cases is very slightly soluble in ether and the reagent is pasty. Well-conducted preparations of this reagent, which contained but little precipitate, when analyzed showed that about 50% of the magnesium had been converted into a Grignard reagent.

A. Grignard Reagents and Aldehydes

Acetaldehyde and *Tert.*-**butylmagnesium** Chloride.—Eleven grams (0.25 mole) of freshly distilled acetaldehyde dissolved in 50 cc. of ether was added to a theoretical 8 moles of *tert.*-butylmagnesium chloride. After working up, the ether was removed on the steam-bath and the residual material fractionated. There was obtained 1.3 g. of low-boiling material (85–115°), then 20.5 g. boiling at 115–119°, mostly at 116–118°, a yield of 80%. The residue was less than 1 cc. The main fraction, methyl-*tert.*-butylcarbinol, gave with phenyl isocyanate the well-known phenylurethan,[19] m. p. 75–76°.

Isobutyraldehyde and *Iso*propylmagnesium Bromide.—Pour-tenths of a mole (28.8 g.) of freshly distilled isobutyraldehyde in 50 cc. of ether was added to a theoretical 0.7 mole of isopropylmagnesium bromide. After removing the ether the residue, on fractionation, yielded 3 *g.* of low-boiling material (80–133°) and 36 g. of di-*iso*propylcarbinol, 134–138°; yield, 78%.

With phenyl isocyanate the di-isopropylcarbinol set to a solid mass. This phenylurethan crystallized from ether and petroleum ether in splendid long needles melting at 96–99°.

Anal. Calcd. for $C_{14}H_{21}O_2N$: C, 71.5; H, 8.9. Found: C, 71.6; H, 9.0.

Isobutyraldehyde and *Tert.*-**butylmagnesium Chloride.**[20]—Sixty-five grams (0.9 mole) of freshly distilled isobutyraldehyde in 100 cc. of ether was added to a theoretical 2.2 moles of *tert.*-butylmagnesium chloride. After removing the ether on the steam-bath the residual material was fractionated. On the fourth fractionation the following fractions were obtained: (1) 50–100°, 4.5 g.; (2) 106–114°, 13 g.; (3) 115–145°, 2.4 g.; (4) 148–152°, 57 g. The residue was less than 1 cc.

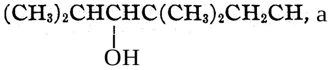
Fraction 2 consisted of isobutyl alcohol for with phenyl isocyanate it yielded within five minutes a solid cake of the phenylurethan of that alcohol.[21] The melting point of the phenylurethan and the mixed melting point with a known specimen was 85–86°; yield of reduction product, 20%.

Fraction- 4 consisted of *iso*propyl-*tert.*-butylcarbinol. With phenyl isocyanate it yielded the phenylurethan, m. p. 89°. This melting point, confirmed with other specimens, is exactly 10° higher than that given by Haller and Bauer,[22] yield of addition product, 44%. We could find none of the glycol which previously was reported to be formed in this reaction.

---

[19] Delacre, Bull. *soc. chim.*, [4] 1,460 (1907).

[20] Faworsky, J. *prakt. Chem.*, [2] 88, 652 (1913), carrying out this same reaction, obtained 25% addition, 25% condensation and reduction to yield the glycol,



$(CH_3)_2CH\underset{\overset{|}{OH}}{C}HC(CH_3)_2CH_2CH$, and 50% reduction to isobutyl alcohol.

[21] Mylius, Ber., 5, 973 (1872); Blaise and Piccard, Ann. *chim. phys.*, [8] 26, 279 (1912).

[22] Haller and Bauer, *ibid.*, [8] 29,317 (1913).

B. Grignard Reagents and Ketones

Diethyl Ketone and *n*-**Butylmagnesium** Bromide.—Forty-three grams (0.5 mole) of diethyl ketone in 100 cc. of ether was added to a theoretical 1.0 mole of *n*-**butyl**magnesium bromide. The reaction mixture yielded on fractionation 6 g. of material boiling from 106–113°, 2.5 g. boiling from 113–115" and 46 g. boiling at 119–121" at 110 mm. and 116–118" at 105 mm. This last fraction consisted of *diethyl-n-butyl carbinol,* yield, 60%; d_4^{20}, 0.8409; n_D^{20}, 1.4360; M_D, calcd. for n^2 formula, 45.05; n formula, 74.44. Found: n^2 formula, 44.79; n formula, 74.65.

Anal. Calcd. for $C_9H_{20}O$: C, 75.0; H, 13.9. Found: C, 74.7; H, 14.2.

The fraction boiling at 113–115° was heated with 3,5-dinitrobenzoyl chloride and pyridine. No dinitrobenzoate of diethylcarbinol was formed.

In order to secure a solid derivative of diethylcarbinol for identification we had previously treated a known sample of this carbinol with phenyl isocyanate. A solid phenylurethan was not formed. Consequently we had recourse to 3,5-dinitrobenzoyl chloride and pyridine. These yielded the 3,5-dinitrobenzoate of diethylcarbinol which melted, after crystallization from methyl or ethyl alcohol, at 101°.

Anal. Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.1; H, 5.0. Found: C, 50.5; H, 5.1.

Diethyl Ketone and *Tert.*-**butylmagnesium** Chloride.—Four-tenths of a mole (34.4 g.) of diethyl ketone in 100 cc. of ether was added to a theoretical 1.0 mole of *tert.*-butylmagnesium chloride. On fractionation, the reaction mixture yielded 1.3 g. of material boiling from 70–105°, 10 g. boiling from 105–120° and 20 g. boiling from 30–100° at 5 mm. From this material no definite products could be isolated.

Pinacolone and n-ButylmagnesiumBromide.—Fifty grams (0.5 mole) of pinacolone was added to a theoretical 1.0 mole of n-butylmagnesium bromide. On fractionating the reaction product there was obtained 5.5 g. of material boiling from 95–117°, 16 g. boiling from 117–119" and 20 g. boiling from 84–87' at 13 mm. This last fraction was *methyl-n-butyl-tert.-butylcarbinol,* yield, 25%; d_4^{20}, 0.8487; n_D^{20}, 1.4409; M_D, calcd. from n^2 formula, 49.65; from n formula, 82.09. Found: n^2 formula, 49.16; n formula, 82.09.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 13.9. Found: C, 75.6; H, 14.1.

The fraction boiling at 117–119° was shown to be the reduction product of pinacolone, pinacoline alcohol, by conversion to the phenylurethan, m. p. 79°, and a mixed melting point with a known specimen. The yield of reduction product was 30%.

Piacolone and *Iso*propylmagnesium Bromide.—Twenty-five grams (0.25 mole) of pinacolone was added to a theoretical 0.5 mole of isopropylmagnesium bromide. Much gas was evolved. On fractionation there was obtained 13 g. of material boiling from 105–115° and 8 g. of high-boiling material. The low-boiling material yielded no phenylurethan, but with hydroxylamine gave an oxime, m. p. 75°, which was identified as pinacolone oxime by comparison with an authentic specimen,[23] yield of recovered pinacolone, 50%. The high-boiling material on distilling in vacuo boiled at 60–95° at 3 mm. and evidently consisted of condensation products, for methyl-*iso*propyl-*tert.*-butylcarbinol (see later) boils at 56° at 6 mm.

Pinacolone and *Tert.*-**butylmagnesium** Chloride.—Thirty-five grams (0.35 mole) of pinacolone was added to a theoretical 1 mole of *tert.*-butylmagnesium chloride and the product fractionated twice. There was obtained 22 g. of material boiling at 100–117°, and 9.4 g. of high-boiling material. This latter consisted of condensation products, for on distillation in vacuo it boiled over a wide range, 65–100° at 5 mm. The material boiling at 100–117° was shown to be recovered pinacolone by the preparation from it of benzalpinacolone, m. p. 41–42°.[24]

---

[23] Janny, Ber., 15,2780 (1882).

[24] "Organic Syntheses," John Wiley and Sons, Inc., Mew York, 5, 15 (1926).

Isobutyrone and *n*-**Butylmagnesium** Bromide.—From **57** g. (**0.5** mole) of *iso*-butyrone and a theoretical mole of reagent there was obtained on fractionation a small amount of low-boiling material, then **3** g. boiling from 128–137°, **8** g. boiling from 137–140° and **34** g. boiling at **115–118°** at **45** mm. This last fraction, consisting of di-*isopropyl-n-butyl carbinol,* which was obtained in a yield of **40%;** d **0.8487;** and n^{20}_{D}, 1.4435; M_D, calcd. from n^2 formula, 54.26; from n formula, 89.84. Found: n^2 formula, **53.78;** n formula, **89.86.**

Anal. Calcd. for $C_{11}H_{24}O$: C, **76.7;** H, **14.0.** Found: C, **76.6;** H, **14 2.**

The material boiling at 137–140° was shown to be di-isopropylcarbinol by conversion to the phenylurethan and mixed melting point with a known sample The yield of this reduction product was **13%.**

Isobutyrone and Isopropylmagnesium **Bromide.**[25]—From **28.5** g. (**0.25** mole) of isobutyrone and a theoretical **0.5** mole of isopropylmagnesium bromide, there was obtained **2.4** g. of material boiling from 80–134°, then **22.5** g. boiling at 135–138° and **3** g. boiling from 138–143°. The residue amounted to **2** cc. The fractions boiling at 135–138° and 138–143° consisted of di-isopropylcarbinol, for with phenyl isocyanate they set to a solid mass of phenylurethan, m. p. **95".** The identity of this phenylurethan was established by a mixed melting point. The yield of reduction product was 78%.

Isobutyrone and *Tert.*-**butylmagnesium** Chloride.—From 28.5 g. (**0.25** mole) of isobutyrone and a theoretical **0.8** mole of *tert.*-butylmagnesium chloride there was obtained **3** g. of material boiling at 70–110°, **2.1** g. boiling at 110–130° and **21.8** g. boiling at **136–138".** The residue amounted to **1** cc. The two latter fractions consisted of the reduction product, di-isopropylcarbinol, for with phenyl isocyanate they yielded the known phenylurethan (melting point and mixed melting point). The yield of reduction product was **80%.**

Pentamethylacetone and **Methylmagnesium** Iodide.—From **26** g. of pentamethylacetone and a theoretical **0 3** mole of methylmagnesium iodide there was obtained 4 g. of low-boiling material and then **18** g. of *methyl-isopropyl-tert-butylcarbinol,* b. p. 56–57° at **6** mm., a yield of 60%. This carbinol has d^{20}_{4}, **0.8564;** n^{20}_{D}, **1.4430.** M_D, calcd. from n^2 formula, **45.05;** from n formula, **74.44.** Found: n^2 formula, **44.59;** n formula, **74.49.**

Anal. Calcd. for $C_9H_{20}O$: C, **75.0;** H, **13.9.** Found: C, **75.2;** H, **13.9.**

In this reaction the intermediate magnesium compound separates as splendid colorless crystals.

Pentamethylacetone and Isopropylmagnesium Bromide.—From **19.2** g. (**0.15** mole) of ketone and a theoretical **0.29** mole of reagent there was obtained **0.8** g. of low-boiling material, to 149°, then **17.1** g. of reduction product boiling at 149–151°. The *iso*-propyl-*tert.*-butylcarbinol, identified through its phenylurethan, was obtained in an 88% yield.

Pentamethylacetone and *Tert.*-**butylmagnesium** Chloride.—From **19.2** g. (**0.15** mole) of ketone and a theoretical **0.5** mole of reagent there was obtained **1.3** g. of material boiling up to 149°, then **17.6** g. of reduction product, boiling at **149–151 .** The reduction product, *iso*propyl-*tert.*-butylcarbinol, yield 90%, was identified as the phenylurethan.

Hexamethylacetone and **Methylmagnesium** Iodide.—From **13** g. of hexamethylacetone and the Grignard reagent prepared from **4** g. of magnesium and **23** g. of methyl

---

[25] This reaction, already carried out by Stas, *Bull. soc. chim. belg.*, 34, **188 (1925); 35,379** (1926), was repeated because from the experimental data given in his article the yield of reduction product (50%) was not as large as we expected in view of our results with *tert.*-butylmagnesium chloride.

iodide there was obtained 11.4 g. of solid *di-tert.-butyl-methylcarbinol,* b. p. 184–191°, m. p. 39–41° and 0.9 g. of low-boiling material; yield, 78%. (The period of refluxing was four hours.)

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.8; H, 14.0. Found: C, 75.4; H, 13.7.

Hexamethylacetone and Isopropylmagnesium Chloride.—From 13 g. of the ketone and the Grignard reagent from 4 g. of magnesium and 13 g. of isopropyl chloride (period of refluxing three and one-half hours) there was obtained 6 g. of unchanged ketone (b. p. 150–159°), 1.5 g. of b. p. 159–161° and 1.2 g. of b. p. 163–167". The last fractions solidified and were identified as di-*tert.*-butylcarbinol.

Hexamethylacetone and *Tert.*-butylmagnesium Chloride.—From 14 g. of the ketone and the Grignard reagent from 6 g. of magnesium and 23 g. of *tert.*-butyl chloride there was obtained (after four hours of refluxing) 9.9 g. of solid di-*tert.*-butylcarbinol, b. p. 159–167°; yield, 69%.

C. Grignard Reagents and Esters

Trimethylacetic Ester and *Tert.*-butylmagnesium Chloride.—One-tenth mole (12 g) of trimethylacetic ester was added to a theoretical 0.6 mole of reagent and the mixture boiled for ten hours. On working up the products there was obtained 9 g. of recovered ester boiling at 116–119°. No hexamethylacetone or *tert.*-butylcarbinol could be found.

Phenylacetic Ester and Isopropylmagnesium Bromide.—Three-tenths of a mole (49.2 g.) of phenylacetic ester was added to a theoretical 0.5 mole of isopropylmagnesium bromide chilled in an ice-bath. There was a steady evolution of saturated gas and the separation of a light gray magnesium compound. After standing overnight the reaction mixture was decomposed and the ether layer on evaporation gave 39.5 g. of crude diphenylacetoacetic ester; yield, 94%. The crude ester melted at 72–75°. After it was triturated in a mortar with cold alcohol, filtered and dried, it melted at 78°. This product may be recrystallized from alcohol with only slight loss.

The ester was identified by a mixed melting point and by the preparation of the pyrazolone on treatment with phenylhydrazine.[16b]

Summary

1. Besides the normal addition of the Grignard reagent to carbonyl compounds, three other reactions—reduction, enolization and condensation—may take place. The occurrence of these reactions has been correlated with the lengthening and branching of the alkyl groups in the carbonyl compound and reagent. The limits of usefulness of the Grignard reaction for synthesizing secondary and tertiary alcohols have been pointed out. The extreme case where no reaction at all takes place has been illustrated.

2. It is shown that ketones containing two secondary groups or one secondary and one tertiary group may be easily and conveniently reduced to the corresponding secondary alcohols with isopropylmagnesium bromide or *tert.*-butylmagnesium chloride.

3. A synthesis of α,γ-diphenylacetoacetic ester based on the enolizing and condensing action of isopropylmagnesium bromide is described.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

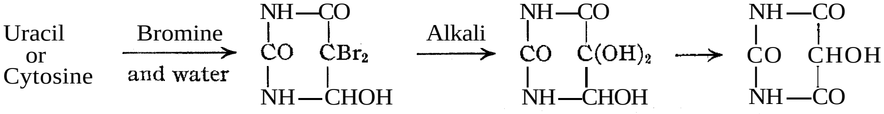
RESEARCHES ON PYRIMIDINES. CV. A NEW TEST FOR THYMINE AND 5-METHYLCYTOSINE IN THE PRESENCE OF URACIL AND CYTOSINE[1]

BY HENRY H. HARKINS[2] AND TREAT B. JOHNSON

RECEIVED NOVEMBER 7, 1928 PUBLISHED APRIL 5, 1929

Introduction

In 1907 Wheeler and Johnson[3] showed that when uracil or cytosine is treated first with bromine water, and then with an alkali, the following reactions take place



$$\begin{array}{l}\text{Uracil}\\ \text{or}\\ \text{Cytosine}\end{array} \xrightarrow[\text{and water}]{\text{Bromine}} \begin{array}{ll} NH & —CO \\ | & | \\ CO & CBr_2 \\ | & | \\ NH & —CHOH \end{array} \xrightarrow{\text{Alkali}} \begin{array}{ll} NH & —CO \\ | & | \\ CO & C(OH)_2 \\ | & | \\ NH & —CHOH \end{array} \longrightarrow \begin{array}{ll} NH & —CO \\ | & | \\ CO & CHOH \\ | & | \\ NH & —CO \end{array}$$

I II III

The dialuric acid formed, III, is characterized by its property of interacting with barium hydroxide to give a purple, insoluble barium salt.

Since 1907 this reaction has been used widely by biochemical workers as a practical test for these two pyrimidines. It was found that thymine, IV, would not give this purple barium salt, a fact which could be predicted from inspection of the structural formula of the pyrimidine. Johnson[4] later described a method for separating thymine from uracil by means of nitric acid, but this method of analysis was not proposed by him as a test for thymine in the presence of uracil. We have available, therefore, delicate tests for uracil and cytosine, and as thymine is also a normal constituent of many nucleic acids, it was very important to develop a correspondingly delicate test for this pyrimidine which would be applicable in the presence of either uracil or cytosine. The object of the research discussed in this paper was to develop, if possible, from known reactions a practical test for thymine which would meet these conditions.

The first attempt to perfect a specific test for thymine was made by Johnson and Baudisch,[5] who made a preliminary study of the oxidation products of thymine. It was found that the thymine molecule, in the presence of the system *ferrous sulfate* + *sodium bicarbonate* + air yields after acid hydrolysis urea, pyruvic acid, acetol and formic acid. Urea

---

[1] Constructed from a dissertation presented by Henry Harvey Harkins, in June, 1927, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Holder of the DuPont Fellowship in Chemistry.

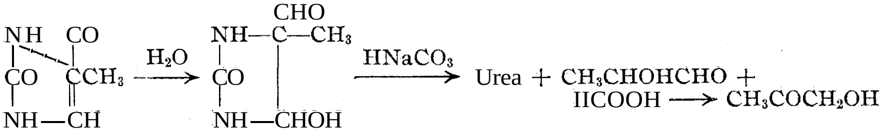
[3] Wheeler and Johnson, J. *Biol. Chem.*, 3, 183 (1907).

[4] Johnson, *Am. Chem J.*, **40**, 19 (1908).

[5] Johnson and Baudisch, THIS JOURNAL, 43, 2670 (1921).

is identified by means of its xanthydrol derivative;[6] the pyruvic acid is converted to the dyestuff indigo by interaction with o-nitrobenzaldehyde, the acetol is identified as 3-oxyquinaldine formed by warming the acetol in alkaline solution with *o*-aminobenzaldehyde,[7] while formic acid is identified by its reducing action on silver nitrate in ammoniacal solution. It was found that pure thymine, IV, in quantities of milligrams only (2 to 5 mg.) may be detected by this procedure. No postulations were made regarding the mechanism of this interesting degradation of the thymine molecule. Deuel and Baudisch[8] later reported a modification of this test for the detection of thymine in the presence of carbohydrates.

This research was continued later by Baudisch and Bass,[9] who investigated the action of other oxidizing reagents on thymine, namely, (1) hydrogen peroxide, (2) hydrogen peroxide + ferrous sulfate, (3) sodium penta-cyano-aquo-ferroate + air, (4) ferrous sulfate + sodium bicarbonate + air and (5) iodine + sodium bicarbonate. They found that the five oxidizing agents except iodine were productive of urea, acetol and pyruvic acid when the products of oxidation are heated in aqueous solution with sodium bicarbonate. Acetol is formed as a direct hydrolytic product of thymine, while pyruvic acid is formed by the hydrolysis of an intermediate oxidation product of unknown constitution. Baudisch and Bass were apparently only interested in the mechanism of these various changes, and interpreted the course of the hydrolytic split of thymine as follows



IV V

With the first three oxidizing reagents the time required to carry out the complete operation is from twelve to forty-eight hours. The following quotation from the paper by Baudisch and Bass[8] reveals their method of oxidizing thymine with iodine "50 cc. of an approximately 0.1 *N* solution of iodine was added to a solution of 0.5 gram of thymine and 30 grams of sodium bicarbonate. The reaction mixture after dilution to one liter was allowed to stand overnight. The excess of iodine was then removed by blowing a rapid stream of air through the solution until it was decolorized (about four hours). The colorless solution was then distilled to a small volume. The distillate gave a strong acetol test. The residue gave a strong test for urea but no test for pyruvic acid. Al-

---

[6] Fosse, *Compt.* rend., 145, 813 (1907).

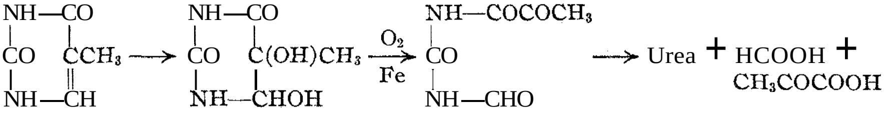
[7] Baudisch, *Biochem.* Z., 89, 279 (1918).

[8] Deuel and Baudisch, THIS JOURNAL, 44, 1581 (1922).

[9] Baudisch and Bass, *ibid.,* 46, 181, 184 (1924).

though this experiment has been repeated several times, a positive test for pyruvic acid has never been obtained." This quotation will serve to illustrate the technique of these tests as compared with that of the simplified test described in detail in the Experimental Part of this paper. Furthermore, the mechanism of change brought about by the action of iodine on thymine is undoubtedly identical in principle with our new procedure, but Baudisch and Bass were not conscious of this at the time of their work.

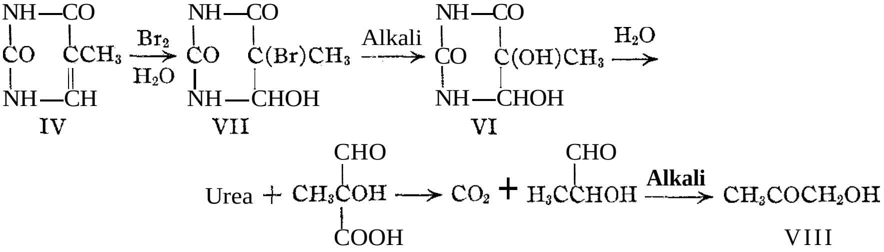
The correct formulation of the mechanism of the oxidation of thymine was worked out by Baudisch and Davidson.[10] They rejected the previous explanation postulated by Baudisch and Bass[8] and concluded that the mechanism of reaction leading to the formation of pyruvic acid is to be explained as follows



IV VI

In other words, they demonstrated that the different end-products resulting from degradation of thymine by oxidation and hydrolysis can result from the breakdown of an intermediate pyrimidine-glycol represented by Formula VI. But here again these workers emphasized only the mechanism of reaction in their work and did not point out any improved applications that could be made of their technique for the testing for thymine in the presence of other compounds. With these data at hand we have now been able to establish the basis of a very sensitive test for thymine applicable in the presence of uracil and cytosine.

Basis of the Thymine Test.—Thymine IV is converted quantitatively into 4-hydroxy-5-bromohydrothymine, VII, by the action of bromine water.[11] Baudisch and Davidson prepared this pyrimidine according to Jones' directions and showed that it undergoes hydrolysis easily with formation of carbon dioxide, acetol and urea. From these two observations we can now formulate reactions which lead to an important and intensively delicate test for thymine. The changes are expressed as follows



IV VII VI VIII

---

[10] Baudisch and Davidson, J. Biol. Chem., 64,233 (1925).

[11] Jones, Z. physiol. Chem., **29,** 20 (1900).

To carry out this simple test one treats thymine in aqueous solution with an excess of bromine and then removes the excess of halogen by boiling the solution. Barium hydroxide is then added in excess and the solution distilled, when acetol is carried over into the distillate. The acetol, VIIX, is then tested for according to the method of Baudisch.[7] The usefulness of this test is apparent if one bears in mind the fact that when uracil and cytosine are treated in a similar manner they both yield almost: quantitatively the purple barium salt of dialuric acid. Therefore, we now have available a procedure whereby these two pyrimidines can be detected easily in the same solution containing thymine, and can be removed from solution so as not to interfere with the acetol test for thymine. The reactions are easy to perform and the tests for the three pyrimidines in the same solution can be applied in a few minutes.

Application of the Acetol Test with **5-Methylcytosine.**—On account of the structural relationship existing between thymine and 5-methylcytosine and between uracil and cytosine, respectively, and since uracil and cytosine are both converted by action of bromine water and alkali into dialuric acid, it was logical to suppose that 5-methylcytosine would give the same end-products as thymine, IV. Experimentally this has been found to be the case and the detection of the four pyrimidines, uracil, thymine, cytosine and 5-methylcytosine, thus becomes a simple matter. The technique of this analytical procedure is discussed in detail in the Experimental Part of this paper. The investigation is being continued.

Experimental Part

Synthesis of Thymine.—Thymine was prepared by hydrolysis of 2-ethylmercapto-5-methyl-6-oxypyrimidine.[12] This mercapto-pyrimidine can be obtained in much better yields than according to the procedure described in the previous paper.

Sodium **Ethylformylpropionate.**—For the preparation of this salt the necessary reagents were used in the following amounts: 204 g. of ethyl propionate, 222 g. of ethyl formate, 1000 cc. of anhydrous ether and 46 g. of sodium. The two esters were mixed and then added slowly through a dropping funnel to ether in which was suspended the sodium. In order to accelerate the reaction the sodium was granulated by melting under the toluene and thoroughly shaking while cooling. The toluene was then decanted, the sodium washed with anhydrous ether and finally covered with dry ether in a large, round-bottomed flask connected to a reflux condenser. The ether solution of mixed esters was then dropped onto the sodium during a period of two days and the mixture allowed to stand for a third day to complete the reaction. Water was then added cautiously and the sodium salt of ethylformylpropionate dissolved. The water layer was separated and used in the condensations described below. Several preparations of this salt were made and in each condensation reaction the water layer was diluted to 1000 cc. and then divided into aliquot parts as required. Seven pyrimidine condensation reactions were then made using salt units corresponding to known weights of ethyl propionate (see Table I).

It may be concluded from the results of these experiments that the addition of

---

[12] Wheeler and Johnson, *Am. Chem.* **J.**, 31, 591 (1904).

alkali is not necessary in this condensation, and also that 102 g. of ethyl propionate is productive of sufficient condensation product—ethyl *sodium formylpropionate*—to interact with only 23 *g.* of pseudo-ethylthiourea hydrobromide (0.125 mole).

TABLE I

CONDENSATIONS WITH PSEUDO-ETHYLTHIOUREA

No.	Pseudo-ethylthiourea hydrobromide, *g.*	Ethyl propionate in form of sodium-formylpropionate, g.	Yield of mercapto-pyrimidine, g.	Sodium hydroxide, g.
1	185 (1 mole)	102	31	None
2	185 (1 mole)	102	26	40
3	92.5 (0.5 mole)	102	30	None
4	92.5 (0.5 mole)	102	20	20
5	46.0 (0.25 mole)	102	31.5	None
6	46.0 (0.25 mole)	102	36.00	None
7	23.0 (0.125 mole)	102	19.00	None

Theoretical yield for (Expt. 7) 31.00 g.

Preparation of **5-Methylcytosine.**—This pyrimidine was synthesized from 2-ethylmercapto-5-methyl-6-oxypyrimidine according to the method described by Wheeler and Johnson.[3] This process involves treatment of the 2-ethylmercaptopyrimidine with phosphorus pentachloride to obtain 2-ethyl-mercapto-5-methyl-6-chloropyrimidine and then heating this chloro compound under pressure with ammonia. The resulting mercapto-aminopyrimidine is then converted into 5-methylcytosine by hydrolysis with hydrochloric acid. Ninety-three grams of the 2-ethylmercaptopyrimidine were productive of 82 g. of the chloro compound boiling at 145–147° at 15–18 mm. By heating this chloride at 125–120° in alcohol saturated at 0° with ammonia nearly a quantitative yield of the corresponding aminopyrimidine was obtained. After digesting this mercaptopyrimidine for six hours with hydrochloric acid the evolution of mercaptan had ceased and on evaporating the solution the hydrochloride of 5-methylcytosine was obtained in excellent yield. Practically no thymine, IV, is produced in this hydrolysis. The free base was separated according to the directions of Wheeler and Johnson.

Application of the Acetol Test with Uracil, Thymine, Cytosine and **5-Methylcytosine:** Thymine.—To 0.0100 g. of pure thymine dissolved in 50 cc. of water, bromine is added until a red color is permanent. The excess of bromine is then removed by boiling and to the solution is added 1.0 g. of barium hydroxide crystals. The mixture is then refluxed for fifteen minutes and then distilled. The distillate is made strongly alkaline with sodium hydroxide and tested for acetol as follows.

"3.0 grams of crystalline *o*-nitrobenzaldehyde is mixed with 50 grams of crystalline ferrous sulfate and to this is added 75 cc. of concentrated aqueous ammonia solution. This ammoniacal solution is then heated on the steam-bath for one hour. It is then distilled with steam and several cubic centimeters of the distillate added to the alkaline solution containing acetol described above. This mixture is then evaporated by heating over a Bunsen flame to a volume of 25 cc. After cooling, hydrochloric acid is added until distinctly acid, and the solution then made alkaline by addition of sodium bicarbonate and the solution filtered. The solution thus obtained shows a deep blue fluorescence even in diffused daylight."[7]

In order to test the delicacy of this reaction successively smaller quantities of thymine were used and the solution containing acetol and *o*-aminobenzaldehyde was evaporated to a small volume, in some cases to a volume of 1 cc. It was observed that a blue fluorescence could be obtained with 0.001 g. of thymine. Although the characteristic fluorescence produced with this small quantity of pyrimidine is not observable in ordinary light, it can easily be seen in the light of a mercury arc lamp.

Baudisch[7] does not mention in his paper how to preserve the o-aminobenzaldehyde reagent. It was found that the aqueous solution containing o-nitrobenzaldehyde, ferrous sulfate and ammonia, heated as described above, could be allowed to stand in the laboratory for two weeks without destruction of the aminobenzaldehyde, *i. e.*, the steam distillate from such a mixture gave the fluorescence characteristic of 3-oxyquinaldine at the end of this time.

Uracil and Cytosine.—From inspection of the formulas of uracil and cytosine it can be seen that neither of these pyrimidines can give rise to acetol when treated with bromine and alkali. Uracil prepared by the hydrolysis of 2-methylmercapto-6-oxypyrimidine, when tested for acetol was found, however, to give a distinct, blue fluorescence, which persisted even when the uracil thus obtained was recrystallized several times from water. The same quantity of synthetic cytosine made by the pseudothiourea method3 was also found to give a distinct fluorescence. Apparently these pyrimidines contained a small trace of thymine and 5-methylcytosine, respectively, as impurity. The presence of these two impurities can be traced back to the original aliphatic ester used in the first condensation of the synthesis, namely, ethyl acetate. It is necessary that this reagent be absolutely free from ethyl propionate in order to obtain uracil or cytosine that will not respond to the acetol test.

In order to prove that uracil, when free from thymine, will not give the acetol test, this pyrimidine was synthesized from urea and malic acid according to the method of Davidson and Baudisch.[13] The uracil so obtained cannot contain thymine When 0.5 g. of this product was tested for acetol no fluorescence whatever could be detected thereby proving that uracil and cytosine cannot produce the blue fluorescence characteristic of thymine.

5-Methylcytosine.—5-Methylcytosine hydrochloride prepared as described above responds to the acetol test strongly. In order to make certain, however, that the test in this case is due to 5-methylcytosine and not to thymine, the methylcytosine was precipitated repeatedly as its phosphotungstate and the recovered methylcytosine then tested for acetol as before. A strong fluorescence was obtained, showing that 5-methylcytosine undergoes the same reaction with bromine and alkali as thymine. This is to be expected since uracil and cytosine yield the same product—dialuric acid—when treated with bromine and alkali.

Summary

1. An improved chemical or color test for detecting thymine, based on the experimental work of Johnson, Baudisch and co-workers, has been described.
2. The test is dependent on the formation of acetol by action of bromine and alkali on thymine.
3. The test applies equally well to 5-methylcytosine.
4. Both of these pyrimidines can be detected in quantities as small as one milligram.
5. The acetol test for thymine and 5-methylcytosine is applicable in the presence of uracil and cytosine.

NEW HAVEN, CONNECTICUT

---

[13] Davidson and Baudisch, THIS JOURNAL, 48, 2379 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

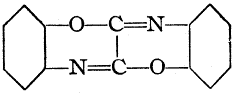
CONDENSATION OF ORTHO-AMINOPHENOL AND OXALIC ACID. PRELIMINARY COMMUNICATION[1]

BY ARTHUR A. LEVINE AND LESTER WEHMHOFF

RECEIVED NOVEMBER 9, 1928 PUBLISHED APRIL 5, 1929

In an investigation undertaken in this Laboratory it was desirable to prepare a number of substituted oxanilides of the general formula $XC_6H_4NHOCCOHNC_6H_4X$. These substances were prepared by fusing the substituted amine with the required quantity of oxalic acid and in each case the desired product was obtained. If o-aminophenol and oxalic acid were used, o-hydroxy-oxanilide was not obtained but another substance was formed melting at 271–272°. This new condensation product possesses a deep red color and will be designated as the "red condensation product."

o-Aminophenol condenses readily with monocarboxylic acids, giving benzoxazoles or β-substituted benzoxazoles depending on the acid used.[2] Kehrmann and Bener[3] have shown that oxalic acid reacts with *o*-aminophenol hydrochloride dissolved in molten benzoic acid, giving a product melting at 260" to which is ascribed the formula



Discussion

The red condensation product is formed on heating a mixture of two moles of o-aminophenol with one mole of anhydrous oxalic acid at 180–200" for thirty minutes. Two moles of water are evolved in the reaction and a small quantity of carbon dioxide (0.04 mole) due probably to partial decomposition of some oxalic acid. If the reaction was carried out at 130–140°, a small quantity of o-hydroxy-oxanilide was formed together with large amounts of the red product. At the higher temperature oxanilide could not be found in the reaction product.

Analysis of the red condensation product gave on calculation the same formula as for o-hydroxy-oxanilide ($C_{14}H_{12}O_4N_2$). Though certain reactions indicate that the molecular weight must be doubled, a direct determination of this has not been possible, as every effort failed to give concordant results due to the slight solubility in the solvents tried.

---

[1] Abstracted from a thesis by L. H. Wehmhoff presented to the Graduate Faculty of the State College of Washington in partial fulfilment of the requirements for the degree of Master of Science.

[2] Ladenburg, *Ber.*, 9, 1524 (1876); 10, 1124 (1877).

[3] Kehrmann and Bener, *Helv. Chim. Acta*, 8, 16 (1925).

If the red condensation product is heated a few degrees above its melting point decomposition occurs, giving carbon dioxide equivalent to one free carboxyl group and a tarry substance which could not be purified. On heating it to a higher temperature the red product decomposes completely into carbon dioxide, water, o-aminophenol and an unidentified substance melting above 300°.

With an alcoholic solution of sodium hydroxide, the red product forms *a* crystalline sodium salt. Analysis of this compound indicates that two atoms of sodium have entered the molecule. The sodium salt on treatment with dimethyl sulfate and an additional quantity of sodium hydroxide gives a crystalline substance containing three methyl groups.

The compound reacts with one molecule of aniline with the elimination of a molecule of water and the formation of a new substance. It gives an acetyl derivative by the action of acetic anhydride or acetyl chloride, which gradually decomposes on recrystallization from benzyl alcohol and yields the diacetate of o-hydroxy-oxanilide.

The red condensation product is not affected by acids but it is readily decomposed by alkalies. Toward oxidizing and reducing agents in an acid medium it is stable. Alkaline reducing agents such as zinc dust and sodium hydroxide convert it into a colorless, unstable reduction product which has not yet been obtained in a pure state.

Experimental

Numerous experiments were performed in order to determine the most suitable conditions for the formation of the red product. In some of these trials the relative quantities of o-aminophenol and oxalic acid were varied and in others the temperature at which the reaction was carried out. The following procedure has been found to be the most suitable.

One mole of oxalic acid and two moles of o-aminophenol were intimately mixed and transferred to an Erlenmeyer flask. This was immersed in an oil-bath and maintained at 180–200° for about one-half hour. The grayish red reaction product was pulverized and washed with dilute hydrochloric acid and water. The impure product (yield, quantitative) melted at 250–260°. It was crystallized first from nitrobenzene and subsequently from benzyl alcohol until a pure substance melting at 271–272° was obtained.

Anal. Subs., 0.2320, 0.3490: CO_2, 0.5270, 0.7934; H_2O, 0.0918, 0.1377. Subs., 0.4676, 0.2854: 33.05, 20.25 cc. of 0.1053 N acid. Calcd. for $C_{28}H_{24}O_8N_4$: C, 61.74; H, 4.44; N, 10.29. Found: C, 61.97, 62.02; H, 4.43, 4.42; N, 10.42, 10.46.

Properties of the Red Product.—It crystallizes in small, red plates from dimethylaniline, nitrobenzene and benzyl alcohol. It is insoluble in most solvents. It dissolves in concentrated sulfuric acid, from which it reprecipitates unaltered on addition of water. Concentrated and dilute alkalies on heating decompose it. On acidifying an alkaline solution that has been heated, carbon dioxide is evolved and a tarry substance is formed.

Determination of the Carbon Dioxide Evolved on Heating the Red Product to 280°.—A weighed quantity was heated in an Erlenmeyer flask immersed in an oil-bath maintained at a temperature of 280° for one hour. The flask was connected with a U-tube containing concentrated sulfuric acid and this to a weighed potash bulb. A slow current of air was passed through the apparatus.

Anal. Subs., 2.6420, 2.0300: CO_2, 0.2077, 0.1700. Calcd. for one carboxyl in $C_{28}H_{24}O_8H_4$: 8.09. Found: 7.86, 8.37.

Heating the substance to 320° decomposes it completely into carbon dioxide, water, o-aminophenol and an unidentified substance melting above 300".

The Sodium Salt of the Red Condensation Product.—This is formed on carefully warming the red product with an excess of 0.5 N alcoholic solution of sodium hydroxide. Long, needle-like crystals formed. These were recrystallized five times from 80% alcohol containing a small quantity of sodium hydroxide. The amount of sodium was determined by treating a weighed quantity with sulfuric acid and oxidizing the organic matter with nitric acid. Though somewhat high values were obtained, the results indicate that two atoms of sodium had reacted.

Anal. Subs., 0.2807, 0.7638: Na_2SO_4, 0.0775, 0.2026. Calcd. for $C_{28}H_{22}O_8H_4Na_2$: Na, 7.82. Found: Na, 8.94, 8.59.

The corresponding potassium salt was also prepared but was found to be even more difficult to crystallize. Both the sodium and potassium salt decompose readily on heating in aqueous or alcoholic solutions.

The Aniline Derivatives of the Red Product.—Ten grams of the red product were refluxed for one hour with 50 cc. of aniline. The resulting solution deposited well-formed crystals on standing. These were recrystallized from dimethylaniline and subsequently from nitrobenzene. The purified compound melts at 250°.

Anal. Subs., 0.2425, 0.1960: CO_2, 0.5850, 0.4724; H_2O, 0.1048, 0.0879. Subs., 0.4237, 0.2766: 31.18, 20.58 cc. of 0.1053 N acid. Calcd. for $C_{34}H_{29}O_7N_5$: C, 65.88; H, 4.72; N, 11.30. Found: C, 65.81, 65.75; H, 4.80, 4.98; N, 10.85, 10.97.

From this it follows that one mole of aniline has reacted with one mole of the original product. The aniline derivative is difficultly soluble in most organic solvents, though readily soluble in benzyl alcohol, nitrobenzene, aniline and dimethylaniline. It is not soluble in concentrated acids or alkalies.

Methyl Ester of the Red Condensation Product.—This was prepared by dissolving 10 g. of the product in 150 cc. of *2* N sodium hydroxide and adding 30 cc. of dimethyl sulfate in small portions with constant shaking. After about one-half of the dimethyl sulfate had been added, a crystalline precipitate formed. When all of the dimethyl sulfate had been added, the reaction mixture was heated on the water-bath for one hour. The product was recrystallized from benzyl alcohol until a constant melting point of 246–247° was attained.

Anal. Subs., 0.2245, 0.2832: CO_2, 0.5216, 0.6562; H_2O, 0.1118, 0.1351. Subs., 0.2240: 13.66 cc. of 0.1053 N acid. Calcd. for $C_{31}H_{30}O_8N_4$: C, 63.45; H, 5.33; N, 9.38. Found: C, 63.36, 63.20; H, 5.53, 5.36; N, 9.00.

The Acetyl Derivative.—Ten grams of the red condensation product was refluxed for four hours with 200 cc. of acetic anhydride. The acetic anhydride was distilled leaving a residue of about 50 cc. in the flask. This solidified on standing for a short time. The resulting product was transferred to a suction funnel and washed with about 10 cc. of glacial acetic acid, alcohol and finally with ether. The yield of impure product was 6.7 g. melting at 189°. Recrystallization from glacial acetic acid did not change the melting point. From this solvent it precipitates in well-shaped, red-colored plates, quite soluble in acetic acid, nitrobenzene and benzyl alcohol. Analysis for carbon and hydrogen gave values indicating that the substance was not pure. It was recrystallized from benzyl alcohol giving needle-like crystals lighter in color and melting at 183°. Evidently heating the substance with benzyl alcohol caused decomposition. Subsequent crystallization from the same solvent gave finally a perfectly white product, melting at 194°. This white substance is the diacetate of *o*-hydroxy-oxanilide, identified by analysis and a mixed melting point with a synthetic sample prepared by the method of Meyer and Seeliger.[4] These investigators give 201° as the melting point of the diacetate. This melting point is too high; a purified sample melted at 194° (corr.).

Anal. Subs., 0.2002, 0.1891: CO_2, 0.4461, 0.4203; H_2O, 0.0816, 0.0796. Calcd. for $C_{18}H_{16}O_6N_2$: C, 60.67; H, 4.50. Found: C, 60.77, 60.61; H, 4.52, 4.73.

The red acetate may be decomposed by dissolving in benzyl alcohol and heating for **a** few minutes. The solution is completely decolorized.

Summary

A new condensation product of o-aminophenol and oxalic acid has been isolated and some derivatives of it are described.

PULLMAN, WASHINGTON

!CONTRIBUTION PROM TEE CHEMICAL LABORATORY OP HARVARD UNIVERSITY]

TRIMETHYLACETALDEHYDE AND DIMETHYLETHYLACETALDEHYDE

BY J. B. CONANT, C. N. WEBB AND W. C. MENDUM

RECEIVED NOVEMBER 13, 1928 PUBLISHED APRIL 5, 1929

Now that tertiary butyl and tertiary amyl alcohols are available, it becomes possible to prepare trimethylacetaldehyde and dimethylethylacetaldehyde in quantities suitable for synthetic work. These aldehydes promised to be of interest in connection with the study of highly-branched compounds which is being carried on in the Harvard Laboratories. In this paper we shall describe the preparation and behavior of these aldehydes in certain reactions. Although the hope of using these substances as a starting point in the synthesis of other branched compounds now seems dim, the results which have come to light are of some general interest.

The procedure we employed in the preparation of both aldehydes is outlined below

$$R_3COH \xrightarrow{HCl} R_3CCl \longrightarrow R_3CMgCl \xrightarrow{HCHO} R_3CCH_2OH \longrightarrow R_3CCHO + H_2$$

The last step, the dehydrogenation, is the same as that employed by Franke[1] in the most recent synthesis of trimethylacetaldehyde. We followed Bouveault's procedure instead of Franke's, however, and using copper at 250–300° obtained a 64–66% yield of aldehyde from both primary alcohols. The yield from the tertiary alcohol to the primary alcohol in both series was 40–50%, making the over-all yield for the four steps given above 25–33%.

---

[4] Meyer and Seeliger, ***Ber.***, 29, 2644 (1896).

[1] Franke and Hinterberger, *Monatsh.*, 43, 657 (1922).

One rather unexpected result was encountered in the preparation of the primary alcohols. If a considerable excess of gaseous formaldehyde is passed into the Grignard reagent, the reaction mixture decomposed and the product isolated in the usual way, as much as two-thirds of the product may be the acetal, $H_2C(OCR_3)_2$. The acetals are high-boiling liquids from which the tertiary alcohols may be obtained by heating with alcoholic hydrochloric acid. Although they are not appreciably decomposed by distillation with steam from 30% sulfuric acid, they appear to be decomposed to some extent by steam distillation of the reaction mixture. This procedure, together with a careful control of the amount of formaldehyde, results in relatively little high-boiling material and the maximum yield of carbinol. An alternative scheme is to employ an excess of formaldehyde and then boil the entire crude product with alcoholic hydrochloric acid, thus regenerating the carbinol from the acetal.

Dimethylethylacetaldehyde was prepared by Faworski[2] with very poor yields by chromic acid oxidation of the primary alcohol. Our product yielded a semicarbazone with the same melting point as that reported.

Autoxidation and Photochemical Decomposition.—Both trimethylacetaldehyde and dimethylethylacetaldehyde rapidly undergo autoxidation in the air. Samec[3] has shown that the final product in the first case is trimethylacetic acid and we have obtained as much as 82% of dimethylethylacetie acid by the autoxidation of the corresponding aldehyde. The phenomenon of the autoxidation of both these aliphatic aldehydes seems to be very similar to the autoxidation of benzaldehyde. After a short exposure to air, peroxide is present, as shown by the liberation of iodine from acidified potassium iodide solution. If a sample of aldehyde containing the peroxide is allowed to stand out of contact with air, the peroxide disappears, presumably because it is used up in the oxidation of a further amount of the aldehyde to acid. The autoxidation is retarded by the presence of hydroquinone. This was determined by following the process of oxidation by the titration of the acid formed; it was also found that the peroxide developed much more slowly. Although the rate of oxidation of pure trimethylacetaldehyde is of the same order of magnitude as that of pure benzaldehyde, the effect of the hydroquinone is much greater on the aromatic substance.

It was noticed early in our work that the liquid aldehyde slowly evolved gas and the evolution proceeded more rapidly in diffused daylight than in the dark. As much as 30 cc. of gas was evolved from 40 g. of aldehyde in the course of a day. The gas was found to be carbon monoxide. The

[2] Faworski, J. *Russ. Phys.-Chem. Soc.*, **50**, 43 (1918), Chem. Zentr., III, 667 (1923); Bouveault, *Bull. soc. chim.*, [3] 31, 1326 (1904), obtained the compound in traces and analyzed the semicarbazone.

[3] Samec, *Ann.*, 351, 259 (1907).

decomposition of aliphatic aldehydes by the action of ultraviolet light according to the equation $RCHO \longrightarrow RH + CO$ has been studied by Franke and Pollitzer.[4] The action of ultraviolet light on trimethylacetaldehyde was shown by Hinterberger[5] to cause the evolution of carbon monoxide, presumably as a result of the same reaction. We have been able to show that this is, indeed, the case since we isolated *iso*butane from a sample of pure trimethylacetaldehyde which was allowed to decompose for many weeks in daylight in the absence of oxygen.

A few preliminary experiments were performed to outline in a general way the photochemical behavior of these trisubstituted aldehydes. About 40 g. of aldehyde was employed and the rate of gas evolution per hour measured when illuminated by a quartz mercury arc lamp. The rate of decomposition was about the same in both quartz and pyrex flasks but was reduced to one-half by the interpolation of 1.45 mm. of soft glass and to about 20% by 1 mm. of mica. These facts enabled us to estimate the range of effective light from an inspection of photographs of the iron arc which were taken through our pyrex flask, glass plate and mica sheet. We are indebted to Mr. W. C. Root for these spectrograms. The limits of transmission were: pyrex, 2950 Å.; mica, 3020 Å. (3020 to 3150 Å. weak); glass, 3100 Å. (3100 to 3150 Å. weak). Since pyrex and quartz were photochemically equivalent in our reaction, whereas both mica and glass greatly diminished the effectiveness of the light, we conclude that it is primarily light of a wave length of 2950 to 3200 Å. that is responsible for the photochemical decomposition of trimethylacetaldehyde.

It is a well-known fact that the autoxidation of benzaldehyde is accelerated by ultraviolet light and we found a two-fold increase in the autoxidation of trimethylacetaldehyde when it was exposed to a quartz mercury arc. It is an interesting question for further research to decide what connection, if any, exists between the autoxidation reaction and the decomposition into carbon monoxide. That there is some connection is suggested by the facts just mentioned and also by our observation that the addition of 1 part in 500 of hydroquinone decreases to a third the photochemical decomposition in ultraviolet light.

Cannizzaro Reaction.—Although the Cannizzaro reaction is often supposed to be a general reaction of aldehydes which have no hydrogen in the a-position, Hinterberger[5] could obtain no evidence of this reaction with trimethylacetaldehyde. He used a concentrated solution of potassium hydroxide in water and some alcohol. Using 50% alcoholic potassium hydroxide containing a little water we obtained, after letting the homogeneous solution stand for one day at room temperature, a 59% yield of the carbinol and 55% yield of the acid. The Cannizzaro reaction

---

[4] Franke and Pollitzer, *Monatsh.*, 34, 797 (1913).

[5] Hinterberger, "Dissertation," Vienna, 1923.

thus does proceed with this aldehyde to at least 60% if alcohol is used as a mutual solvent for the alkali and the aldehyde. When we used aqueous alkali, however, we obtained chiefly unchanged aldehyde and indefinite higher boiling condensation products.

The Action of the Grignard Reagent.—The usual addition reaction between the Grignard reagent and an aldehyde is complicated in the case of aldehydes of the type R_3CCHO by the appearance of a reduction reaction which leads to the carbinols R_3CCH_2OH. Which of these two competing reactions predominates is determined by the nature of the hydrocarbon residue attached to the magnesium atom of the Grignard reagent. Thus with n-propylmagnesium bromide and dimethylethylacetaldehyde 15% reduction was observed, with isopropylmagnesium bromide 33% and with *tert.*-butylmagnesium chloride the reduction was 65%; in this last case there was no evidence of an addition reaction. With trimethylacetaldehyde, the process of reduction is slightly less pronounced than with its homolog; thus with the n-propyl Grignard reagent there was only a trace of reduction as compared with 15% with dimethylethylacetaldehyde, and the yield of addition product was 50% against 45%. With isopropylmagnesium bromide the figures were: trimethylacetaldehyde, reduction 10%, addition 33%; dimethylethylacetaldehyde, reduction 33%, addition 27%. The distinction between the two aldehydes thus seems to be just sufficient to be detected by our methods. Similar results have been obtained in this Laboratory in a study of the action of the Grignard reagent on ketones[6] and it is not necessary in this paper to discuss again this interesting effect of branching the chain in carbonyl compounds and Grignard reagents.

Experimental

(A) Preparation of **Trimethylacetaldehyde.**—*Tert.*-butylcarbinol was prepared from *tert.*-butylmagnesium chloride[7] and formaldehyde by a modified Courtot procedure.[8] The directions for the preparation of cyclohexylcarbinol by this procedure are given in detail in a recent volume of "Organic Syntheses"[9] and need only be briefly referred to here. Three moles of Grignard reagent was prepared and the passing in of the formaldehyde vapor required five to six hours. Some difficulty was encountered by the clogging of the entrance tube with solid paraformaldehyde. This was overcome by using a T-tube and running a rod down from time to time. The reaction mixture was hydrolyzed with dilute sulfuric acid, steam distilled and the carbinol purified by fractionation through a long column. The yield was 42 to 50% of the theoretical based on the magnesium. The product boiled at 112–114° and melted at 47–49°.

Di-*tert.*-butyl Acetal of Formaldehyde, $H_2C(OC(CH_3)_3)_2$—Small amounts of this substance were obtained as a high-boiling fraction in the *tert.*-butylcarbinol prepared as described above. In one experiment in which 4.2 moles of formaldehyde vapor

---

[6] Conant and Blatt, This Journal, 51, 1227 (1929).

[7] "Organic Syntheses," John Wiley and Sons, Inc., New York, 8, 40 (1928).

[8] Courtot, Bull. *soc. chim.*, [3] 35, 985 (1906).

[9] "Organic Syntheses," John Wiley and Sons, Inc., New York, 6, 22 (1926).

was introduced into the reagent formed from 3 moles of magnesium, the yield of acetal was 40 g. (0.25 of a mole). The acetal distils at 182–185°. It was not affected by steam distillation from 80% sulfuric acid but was converted into *tert.*-butylcarbinol by heating with an equal weight of 95% ethyl alcohol containing 2 cc. of concd. hydrochloric acid.

Anal. Calcd. for $C_9H_{20}O_2$: C, 70.2; H, 12.8. Found: C, 70.3, 70.0; H, 12.4, 12.5.

Dehydrogenation of the Carbinol.—The method of Bouveault[10] was followed. A copper catalyst was placed in a vertical pyrex tube 2 cm. in diameter and 80 cm. long. This was attached directly to the flask containing the carbinol, the contents of which were kept boiling by means of a Bunsen burner. The tube containing the catalyst was heated electrically to a temperature of 250–300°. The vapors after passing from the flask up through the catalyst were fractionated by means of a long spiral column and the higher-boiling portion returned to the flask by means of a tube leading back from the bottom of the fractionating column. By controlling the rate of distillation with reference to the temperature at the top of the column it was possible to obtain a distillate consisting very largely of the aldehyde. On redistillation through a column, aldehyde boiling at 74–76° was obtained in a yield of 60–66%. The copper catalyst prepared according to Bouveault's directions was found satisfactory for the preparation of both trimethylacetaldehyde and dimethylethylacetaldehyde and was used in a number of runs. The catalyst is subject to poisoning rather easily, however, and in subsequent work many attempts to prepare an active catalyst failed for no apparent reason.

(B) Preparation **of Dimethylethylacetaldehyde.**—The *tert.*-amylcarbinol, $(CH_3)_2$-$C(C_2H_5)CH_2OH$, was prepared from *tert.*-amylmagnesium chloride and formaldehyde exactly in the same manner as the *tert.*-butylcarbinol. In preparing the Grignard reagent from *tert.*-amyl chloride it was noticed that if the amount of ether was insufficient a precipitate formed and the mixture became very thick. The following directions were satisfactory for the preparation of 3 moles of reagent. A 3-liter 3-necked flask was fitted with a stirrer, condenser and dropping funnel. Seventy-two g. of magnesium and a little iodine were placed in the flask. About 150 cc. of ether was added, then 30–40 cc. of chloride, with stirring. In a short time a vigorous reaction started, the flask was cooled and about 500 cc. of ether added as fast as possible. When the reaction slowed down the remainders of 1500–1600 cc. of ether and 360 g. of chloride were mixed and added slowly at such a rate that the mixture boiled gently; this required about six hours. The *tert.*-amylcarbinol boiling at 135–138° (Bouveault and Blanc[11] give 135°) was obtained in yields of 40–47%.

Di-*tert.*-amyl Acetal of Formaldehyde, $H_2C(OC_5H_{11}\text{-}tert.)_2$.—This acetal was obtained as a by-product from the preparation of the *tert.*-amylcarbinol. In one run a large excess of formaldehyde was used and the acetal was the principal product (the reaction mixture was not steam-distilled). The acetal distils at 220–224°. On boiling an alcoholic solution of it containing a little concd. hydrochloric acid it is converted into the *tert.*-amylcarbinol; 5 g. yielded 4 g. of carbinol and the presence of an aldehyde in the solution was shown by Schiff's reagent. The compound does not react with any of the following reagents: methylmagnesium iodide in amyl ether, alcoholic potassium hydroxide, phenyl isocyanate, *p*-nitrophenylhydrazine.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 72.2; H, 13.0. Found: C, 71.9, 71.6; H, 12.8, 13.0. *Mol.* wt. by freezing-point method in benzene: calcd. for $C_{11}H_{24}O_2$: 216. Found: 208, 213.

---

[10] Bouveault, *Bull. soc. chim.*, [4] **3**, 119 (1908).

[11] Bouveault and Blanc, *ibid.*, [3] 31, 749 (1904).

Dimethylethylacetaldehyde, $(CH_3)_2C(C_2H_5)CHO$.—The dehydrogenation of the *tert.*-amylcarbinol was carried out in the apparatus described above. The yield of aldehyde which boiled at 101–107° was 60–66%. The boiling point of the pure aldehyde is 104 ± 0.5°; this value was obtained both with a carefully refractionated material and with aldehyde regenerated from the bisulfite compound. The semihydrocarbazone melted at 153–155°, as reported by Faworski and by Bouveault.[2] A crystalline bisulfite compound was formed by shaking the aldehyde with an aqaeous saturated solution of sodium bisulfite also saturated with sulfur dioxide. The aldehyde was regenerated by the action of sodium carbonate solution. The bisulfite compound is oxidized by air rather rapidly.

Anal. Calcd. for $C_6H_{12}O$: C, 72.0; H, 12.0. Found: C, 71.1, 71.2; H, 12.1, 12.2. Refractive *Index*. $n_D^{22°} = 1.3975$; $d_4^{22} = 0.8040$; M_D (n^2 formula) = 29.99. Calcd., 29.92.

(C) **Autoxidation.**—It is known that the product of autoxidation of trimethylacetaldehyde is trimethylacetic acid. To prove that the dimethylethylacetaldehyde forms the corresponding acid the following experiment was made: Five g. of the aldehyde was placed in a 500-cc. flask fitted with a stopcock and full of oxygen. The flask was attached to a manometer. The stopcock was opened from time to time and the pressure read. It was noticed that the pressure in the flask fell considerably during the early part of the reaction. The flask was allowed to stand for twenty-nine days and then the material was removed. The acid content was determined by means of excess standard base and standard acid. It was found to be 82.1% acid by weight. The acid was then distilled. The major portion distilled between 180–188°, the boiling point of the acid being 186°.

The rate of oxidation of trimethylacetaldehyde to acid both in air and oxygen, with and without hydroquinone, was determined. One gram of the aldehyde was placed in a 300-cc. flask containing air or oxygen and from time to time a sample was removed and its acid content determined by dissolving in excess standard base and titrating back with standard acid, using phenolphthalein as an indicator. The inaccuracy of this method is probably in the neighborhood of 1%. The end-point in the case of the samples containing hydroquinone was rather uncertain. The amount of hydroquinone used in the protected samples was about 1 part in 500. The aldehyde employed contained only a trace of acid. Some typical results showing the percentage of oxidation at different times are as follows: (1) trimethylacetaldehyde in oxygen: 1.75 hrs., 44%; 5.75 hrs., 67%; 18.7 hrs., 83%; 24.9 hrs., 88%; 44.2 hrs., 87%—(2) trimethylacetaldehyde containing 1 part in 500 of $C_6H_4(OH)_2$ in oxygen: 1.75 hrs., 9%; 5.75 hrs., *22%;* 18.7 hrs., 57%; 25 hrs., 65%; 43.5 hrs., 73%; 48.75 hrs., 74%—(3) trimethylacetaldehyde in air: 7.75 hrs., 43%; 25 hrs., 60%; 32.25 hrs., 77%—(4) trimethylacetaldehyde with 1 part in 500 of $C_6H_4(OH)_2$ in air: 5 hrs., 3%; 20.75 hrs., 11%.

(D) **Photochemical Decomposition of** the Aldehydes.—When either of the aldehydes was sealed into a flask containing air connected to a manometer it was noticed that the pressure first fell off and then increased. The increase in pressure continued a long time, being continuously observed for over a month. This increase was not noticed when the flask was covered with black paper. The only logical explanation was that either the aldehyde or some oxidation product was being decomposed by light to a gaseous product. To decide this question about 40 g. of aldehyde was placed in a small flask which was connected to a gas buret filled with mercury. The leveling bulb was kept a little above the mercury level in the buret in order to keep a slight pressure on the system and to prevent leaks inward. After the apparatus had stood for a day or so, it was noted that gas came off, the rate of evolution seemingly increasing with time up to a more or less definite maximum. The amount seemed to be greater the brighter the day. It was noted that the gas was evolved whether the gas above it were air or nitrogen and whether or not the aldehyde had peroxide in it. In the case both of trimethyl- and dimethylethylacetaldehyde, amounts of gas as great as 30 cc. were given off in a day from 40 g., although the amount given off was generally much less than this. It was also noted that if the flask were covered with black paper, the evolution of gas stopped. It was also found that addition of hydroquinone stopped the formation of gas. The gas obtained was analyzed from time to time using the regular methods of gas analysis. The gas both from dimethylethylacetaldehyde and trimethylacetaldehyde had about the same composition. A typical analysis is as follows: CO_2, 0.9%; O_2, 1.0%; CO, 76.1%; material soluble in fuming sulfuric acid, 13.1% ; residue incombustible, 8.8%.

A sample of 30 g. of aldehyde which had been giving off gas to a closed system for several weeks (the evolution being most rapid on bright days) was connected to a gas buret through a return condenser and boiled under diminished pressure. About 345 cc. of gas was thus obtained (some air was introduced in connecting the apparatus); of this 7 cc. only dissolved in concd. sulfuric acid. Of the remainder, 25 cc. condensed to a liquid at −40°. This liquid on evaporation yielded a gas which was identified as *iso*butane by its liquefaction point, −9° to −14°, and its failure to react with concd. sulfuric acid or bromine water.

The action of ultraviolet light was studied using a Cooper-Hewitt Lab. Arc 105–125 V, 1 Amp., Type K 210,230. The results could not be exactly duplicated because the conditions and the output of the lamp could not be accurately controlled. It was found that if 38 g. of aldehyde in a pyrex flask was exposed to the rays from the arc located about 3 inches away, the gas evolved in the first hour (the aldehyde being taken from the dark) was approximately 20 cc., or of the order of the amount of gas given off in a day in good sunlight. The rate of evolution greatly increased during the time of exposure and after the light was turned off gas came off for the next half hour at a high rate. If the aldehyde was placed in quartz the amount of gas in the first hour was about 25 cc. The placing of one glass plate of 1.45 mm. thickness in front of the flask cut the amount of gas down to about 14 cc.; more glass plates had little effect. Passing the rays through 0.9 mm. of mica cut the rate down to 5 cc. in the first forty minutes; the use of only 0.17 mm. of mica gave almost the same result. The addition of hydroquinone in the proportion of 1 in 500 decreased the evolution of gas to approximately 8 cc. in the first hour.

(E) The **Action** of the Grignard Reagent.—The general procedure was to prepare the Grignard reagent from magnesium and the alkyl chloride or bromide in the usual way. Usually 0.4 of a mole of alkyl halide in a total of 225 cc. of ether was used. The aldehyde containing a trace of hydroquinone diluted with 4 to 6 times its volume of ether was run into the well-stirred solution of the Grignard reagent kept at 0°. The reaction mixture after standing overnight at room temperature was warmed to the boiling point of ether for about one hour and then decomposed in the usual way with ice-cold dilute sulfuric acid. With those reagents which caused reduction there was a vigorous evolution of gas when the reaction mixture was warmed; this gas was in part unsaturated hydrocarbons, since it decolorized bromine water. The crude product from the decomposition of the reaction mixture was separated as far as possible by fractional distillation through a spiral column of the Widmer type. The presence or absence of carbinols in the fractions was determined by adding phenyl isocyanate and obtaining the crystalline phenylurethans where possible.

The results are summarized below; unless otherwise stated the Grignard reagent in each case was prepared from 0.41 g. atom of magnesium and a slight excess of alkyl halide. There was thus a large excess of reagent in every case.

Trimethylacetaldehyde and n-Propylmagnesium **Bromide.**—0.12 Mole of aldehyde yielded 0.06 mole of $(CH_3)_3CCHOHCH_2CH_2CH_3$, b. p. 151–157"; phenylurethan, m. p. 69–71°.[12] The fraction at 120–151° was only 1 g. and gave a slight amount of the phenylurethan of $(CH_3)_3COH$.

Trimethylacetaldehyde **and *Iso*propylmagnesium Chloride.**—0.12 Mole of aldehyde yielded 0.04 mole of $(CH_3)_2CCHOHCH(CH_3)_2$, b. p. 140–150°, phenylurethan 87–88°.[13] The fraction at 110–125° gave the phenylurethan of $(CH_3)_3CCH_2OH$; a slight intermediate fraction at 125–140° yielded what seemed to be a mixture of the two phenylurethans. Neglecting the primary alcohol in this fraction the amount of reduction product was 0.01 mole.

Trimethylacetaldehyde and ***Tert*.-butylmagnesium Chloride.**—0.3 of a mole of Grignard reagent (by analysis) in 180 cc. of clear ethereal solution and 0.2 mole of aldehyde yielded 0.13 mole of $(CH_3)_3CCH_2OH$, b. p. 110–111°, which solidified. No other product could be found.

Dimethylethylacetaldehyde and ***n*-Propylmagnesium** Bromide.–4.10 Mole of aldehyde gave 0.015 mole of *tert*.-amylcarbinol, b. p. 130–140°, yielding the known phenylurethan, and 0.045 mole of $(CH_3)_2C(C_2H_5)CHOHCH_2CH_2CH$, b. p. 175–180°, 3,5-dinitrobenzoyl ester (from the chloride and pyridine), m. p. 70–71°. There was

---

[12] Haller and Bauer, *Ann. chim. phys.*, [8] 29, 317 (1913). We also synthesized the carbinol in 47% yield from n-butylaldehyde and *tert*.-butylmagnesium chloride.

[13] Haller and Bauer, ref. 12, give the melting point of the urethan as 79°, but this is probably a misprint for 89°, since this is the melting point of a pure sample prepared from the carbinol synthesized from *tert*.-butylmagnesium chloride and isobutyraldehyde.

a slight intermediate fraction. Since the carbinol was unknown it was also synthesized by the action of *tert.*-amylmagnesium chloride on *n*-butyraldehyde; the yield was only 25%. The pure carbinol boils at 177–178° and the phenylurethan is obtained with difficulty. The 3,5-dinitrobenzoyl ester is more useful for identification; it melts at 71.5–72.5°.

Analysis of *Tert.-amyl n-Propylcarbinol.*—Calcd. for $C_9H_{20}O$: C, 75.0; H, 13.9. Found: C, 75.5; H, 13.9.

Dimethylethylacetaldehyde and Isopropylmagnesium **Bromide.**—0.09 Mole of aldehyde yielded 0.030 mole of *tert.*-amylcarbinol, b. p. 133–134°, a small intermediate fraction, and 0.024 mole of *tert.*-amyl-*iso*propylcarbinol, b. p. 167–177° (Haller and Bauer give the b. p. as 170–171°; we were unable to obtain a pure crystalline phenylurethan from our product).

Dimethylethylacetaldehyde **and** *Tert.*-**butylmagnesium Chloride.**—0.05 Mole of aldehyde added to the reagent from 0.11 mole of magnesium yielded 0.03 mole of *tert.*-amylcarbinol, b. p. 130–137°; the higher and lower boiling fractions were very slight.

(F) Cannizzaro Reaction.—Ten g. of trimethylacetaldehyde was stirred with 15 cc. of 95% alcohol, 2 cc. of water and 7 g. of potassium hydroxide (the solution was cooled before the aldehyde was added) for a day. The mixture was homogeneous. The mixture was poured into water and ether extracted; the extract was dried and distilled through a short column. A strong smell of aldehyde was noticed in the ether distillates. The fractions collected were: 110–116°, 2.5 g.; 116–120°, 0.5 g.; residue 0.5 g. Both the 110–116" and the 116–120° fractions became solid in less than ten minutes on treatment with phenyl isocyanate, forming the phenylurethan of *tert.*-butylcarbinol. The potassium hydroxide solution was acidified and extracted with ether. The extract was dried and distilled: 155–163° (most at 159–164°), 3.3 g. or 55%; residue, 0.5 g.

Three attempts to carry out the Cannizzaro reaction with aqueous sodium hydroxide failed. An emulsion of the aldehyde in 50% aqueous sodium hydroxide for a day at room temperature yielded only a trace of *tert.*-butylcarbinol though a small amount of acid was formed. The chief neutral product boiled over a very wide range. Use of 30% sodium hydroxide, while keeping the emulsion stirred for two and one-half days, gave no evidence of carbinol formation and only a trace of acid which might have come from atmospheric oxidation. Evidently in all three cases large amounts of aldehyde remained unchanged and were contaminated with a mixture of higher boiling neutral substances.

Summary

1. A procedure is described for the synthesis of trimethylacetaldehyde and dimethylethylacetaldehyde from *tert.*-butyl and *tert.*-amyl alcohols.

2. Both aldehydes undergo autoxidation in the air. The process is retarded by the presence of traces of hydroquinone.

3. Both aldehydes undergo photochemical decomposition in bright daylight and in light from a mercury lamp. The effective wave lengths appear to be 2950–3200 Å. The products of the reaction are carbon monoxide and the saturated hydrocarbon.

4. The Cannizzaro reaction may be carried out with trimethylacetaldehyde if alcoholic potassium hydroxide is employed.

5. The action of the Grignard reagent from *n*-propyl, isopropyl and *tert.*-butyl halides on the two aldehydes has been studied. The reagent

from the primary and secondary halides gives addition and reduction products; with the *tert.*-butylmagnesium chloride only reduction occurred.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY AND BIOCHEMISTRY, MEDICAL COLLEGE, CORNELL UNIVERSITY]

THE ISOELECTRIC POINT OF CRYSTALLINE UREASE[1]

BY JAMES B. SUMNER AND DAVID B. HAND

RECEIVED NOVEMBER 13, 1928 PUBLISHED APRIL 5, 1929

Introduction

In connection with our study of the properties of crystalline urease[1a] we have been especially interested in finding the isoelectric point inasmuch as it has never been determined for an isolated enzyme. We thought that a knowledge of this value would help to classify urease among proteins, would aid in improving the method of purification and might eventually throw light on the mode of action of the enzyme on urea.

References to the isoelectric points of enzymes are not lacking in the literature and some of these references are contradictory. Some enzymes have been stated to function as ions over the PH range at which they are active; other enzymes have been found to have isoelectric points coinciding with the PH of their optimum activity and consequently they are thought to react best when not ionized. Thus, pepsin was found by Michaelis and Davidsohn[2] to have an isoelectric point at *P*H 2.26. These authors state that pepsin must be positively charged to have a proteolytic effect. Northrop,[3] however, from a study of the distribution of pepsin and chloride and bromide ions between solid gelatin or coagulated egg albumin, concludes that pepsin is a monovalent ion from *P*H 1 to 7. Michaelis[4] states that with invertase the uncharged particles are active, that with trypsin, erepsin, lipase and maltase the anions are the active part, while with pepsin the cation is active. Michaelis and Pechstein[5] have found the isoelectric point of liver catalase to be at *P*H 5.37 and believe that the anions and uncharged particles are active, while the cations are not. Northrop[6] thinks it probable that the isoelec-

---

[1] The work reported in this paper was supported by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1a] J. B. Sumner, J. *Biol. Chem.*, 69, 435 (1926); **70**, 97 (1926); J. B. Sumner and D. B. Hand, *ibid.*, 76, 149 (1928); *Naturwissenschaften*, 16, 9, 145 (1928); J. B. Sumner and R. G. Holloway, J. *Biol. Chem.*, 79, 489 (1928).

[2] L. Michaelis and H. Davidsohn, *Biochem.* Z., **28**, 1 (1910).

[3] J. H. Northrop, J. *Gen. Physiol.*, 7, 603 (1924–1925).

[4] L. Michaelis, *Biochem. Z.*, **60**, 91 (1914).

[5] L. Michaelis and H. Pechstein, *ibid.*, 53, 320 (1913).

[6] J. H. Northrop, J. *Gen. Physiol.*, 6, 337 (1923–1924).

tric point of trypsin is at PH 10.2 and he finds trypsin to exist as a positive monovalent ion from *PH* 10 to 2. On the other hand, Sherman, Thomas and Caldwell[7] have reported that highly purified malt amylase is isoelectric at *PH* 4.3 to 4.5, which coincides with the *Pa* optimum for the action of this enzyme on starch.

Probably most of the enzyme preparations that have been employed to determine isoelectric points were far too impure to yield significant results. The presence of foreign proteins and other colloids must surely mask the ionic behavior of enzymes. It is of interest to note that in 1911 Pekelharing and Ringer[8] found that highly purified pepsin, which had a minimal solubility at *PH* 3.3, showed no direction of migration under the influence of an electric current unless albumin, or albumose, were added, when the enzyme assumed the electrical properties of the added substance. The apparent purity of crystalline urease suggests that its isoelectric point may be determined accurately.

Electrophoresis Experiments.—The first method employed with crystalline urease was that of electrophoresis. We used the Sherman, Thomas and Caldwell[7] modification of the apparatus of Michaelis[9]

The urease was prepared by methods already described and when obtained from meal low in enzyme activity was recrystallized. The media were phosphate, phthalate and acetate buffers, prepared from reagents which had been carefully purified. Cataphoresis experiments were run for periods varying from two to twenty-two hours, using a direct current of 110 volts. Various non-polarizable electrodes were tried in some cases and in others non-polarizable electrodes were not used. The amount of migration was tested by making determinations of the urease activity in all three chambers of the U-tube.

Our results showed that from *PH* 7 to about 5.5 the urease migrated toward the anode, but in solutions more acid than this very little migration occurred. Since urease is a globulin, the lack of migration in the vicinity of what we later showed to be the isoelectric point is probably due to the presence of salts. This property of globulins of being dissolved without electric charge by salts has already been reported.[10] We would have repeated the migration experiments, using urease solutions containing minimal amounts of buffer, but at present we are unable to procure satisfactory jack bean meal.

Precipitation by Phthalate and Lead Ions.—In the electrophoresis experiments the addition of phthalate buffer to urease caused a precipitation at PH 5 to 4. Since determination of the isoelectric point by migration had been unsatisfactory, we decided to find the PH of maximum

---

[7] H. C. Sherman, A. W. Thomas and M. L. Caldwell, THIS JOURNAL, 46, 1711 (1924).

[8] C. A. Pekelharing and W. E. Ringer, *Z. physiol. Chem.*, 75, 282 (1911).

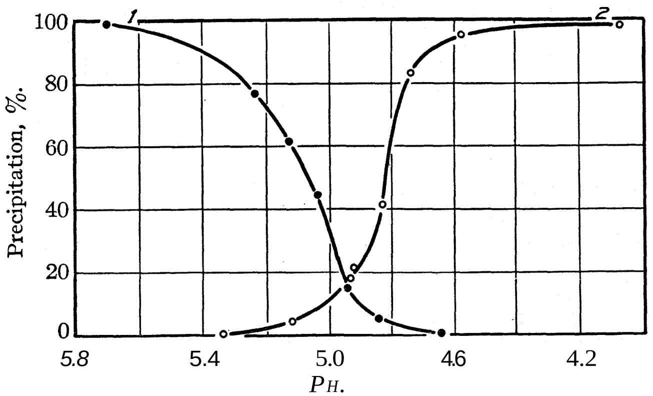
[9] L. Michaelis, *Biochem.* Z., **16**, 81 (1909).

[10] H. Chick, *Biochem. J.*, 7, 318 (1913).

precipitation by phthalate buffer, expecting that this PH could be taken as the isoelectric point.

Experiments were conducted by adding 25 cc. of 0.04 M phthalate buffer, made up at different *PH* values, to 25 cc. of crystalline urease solution, containing 2500 to 3500 units of urease, mixing and allowing to stand in the ice chest for one hour. The material was then centrifuged until the supernatant liquid was water-clear. The centrifuging was continued for intervals of ten minutes with cooling in the ice chest before centrifuging again. In some cases it was necessary to centrifuge for a total of fifty minutes. The supernatant liquid was poured off as completely as possible, and in those cases where either very little, or nearly all of the urease had been precipitated, the centrifuge tube was freed of the last drop of supernatant fluid by a filter paper.

Both supernatant liquid and precipitate were analyzed separately for urease activity. The precipitate was dissolved in dilute neutral phosphate buffer before analyzing. The PH of the supernatant liquid was determined by the quinhydrone electrode. In these experiments very little of the urease was destroyed when the reaction was near PH 5, but at *PH* 4.07 the amount destroyed in one case was 21%. After determination of urease activity and *PH*, the remainder of the material was analyzed for total nitrogen by the macro-Kjeldahl method, using a refined technique suitable for small amounts of material.



1, Precipitation by lead 0.008 M in HAc–NaAc 0.12 M; 2, precipitation by phthalate, 0.02 M.

Fig. 1

The analyses demonstrated that precipitation of urease by phthalate is parallel to the precipitation of the protein and that no significant separation of urease from protein takes place. A curve was constructed, showing the percentage of total urease precipitated with change of PH. We had expected to find a point of maximum precipitation but there was none, as will be seen from Fig. 1. The curve shows that urease begins to precipitate at PH 5.3 and is almost all precipitated at PH 4.6.

Acetate buffer (Walpole's[11] 0.2 *M*) was substituted for the phthalate

---

[11] W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, Maryland, 1927.

buffer in order to study the precipitation of urease in more acid solutions but we were surprised to find the urease to be completely soluble in acetate buffer from *PH* 3.8 to neutrality. We concluded that the precipitation by phthalate is not a *PH* effect solely, but is caused by phthalate ions which unite with positively charged urease.

On account of the results with phthalate we decided to investigate the precipitation of urease with positively charged ions. For this purpose we employed lead acetate, since we had previously observed that lead acetate precipitates urease without much destruction and the insoluble precipitate actively decomposes urea.

The precipitation was carried out by adding to 5 cc. of phosphate-free urease solution, containing about 500 units, 10 cc. of 0 2 *M* acetate buffer, followed by 4 drops of 25.5% lead acetate. The lead acetate was Kahlbaum's and had been recrystallized three times. The material was mixed and allowed to stand for an hour in the ice chest; then it was centrifuged and the ureasc activity determined as was done with the phthalate precipitation. A few experiments were run using larger amounts of enzyme, and analyses for total nitrogen showed that the urease accompanied the protein in its precipitation. Treatment with lead was found to have very little destructive action on urease in the region of PH 5, but in more acid media some destruction occurred. However, even when the addition of lead acetate did not inactivate the urease, centrifuging down the lead precipitate did cause partial inactivation. The way in which the lead precipitate was redissolved apparently made a difference. Here the addition of gum arabic had a favorable effect. In no case in our experiments was more than 25% of the urease inactivated.

A curve was constructed showing the percentage of total urease precipitated with changing *PH*. As will be seen from Table I, urease begins to precipitate under these conditions at *PH* 4.7 and is almost completely precipitated at *PH* 5.6. The curves of precipitation of urease by phthalate and by lead clearly show the amphoteric nature of crystalline urease. On the acid side of *PH* 5 the colloidal particles bear a positive charge and are precipitated by negative ions such as phthalate. On the alkaline side of *PH* 5 the particles are negative and are precipitated by the lead ions. The two curves intersect at PH 4.95 and this value we thought might be taken as the isoelectric point. However, further experiments with lead precipitation have shown that the concentration of lead ions and of acetate buffer have a decided effect. Increasing the amount of lead acetate added was found to push the precipitation more toward the acid side, while increasing the concentration of the acetate buffer dissolved the lead–urease precipitate, or prevented its appearance. Hence it is evident that the accuracy of the isoelectric point established by these two curves can be questioned. The curves do give the isoelectric point approximately and they illustrate the precipitation of urease by certain electrolytes without destruction.

Mercuric and cupric ions precipitate urease over a much wider PH range than do lead ions and unlike lead cause complete inactivation if present in sufficient concentration. Here a portion of the urease can be reactivated by buffered hydrogen sulfide, but all of the urease cannot be reactivated.

Solubility Relationships.—As a result of further experiments we are able to summarize the solubility relationships of urease very simply. Urease is completely insoluble on the alkaline side of the isoelectric point in excess of lead acetate and on the acid side in excess of phthalate buffer. Urease is soluble in excess of phosphate buffer, acetate buffer and carbonic acid–bicarbonate buffer at all *PH* values, but is partly precipitated by these reagents over a narrow *PH* zone, provided a minimal amount of buffer is used. This range lies between *PH* 4.8 and **5.3.** On adding more of the buffer the precipitate immediately redissolves. Hence it is necessary to distinguish between the precipitating action of certain ions, such as lead and phthalate, and that of certain buffers which in small amount are able to precipitate urease by *PH* effect. However, these buffers have a solvent action and if present in sufficient quantity are able to dissolve urease at any *PH*. These findings confirm our previous statement that urease is a globulin.

Determination of Minimal Solubility.—Having an understanding of the solubility relationships of urease, it proved a simple matter to determine the isoelectric point by finding the minimal solubility in greatly diluted acetate buffer.

For this purpose 1-cc. portions of urease solution, containing about 150 units of enzyme, were pipetted into pyrex test-tubes and to each tube was added ***2*** drops of 0.2 *M* acetate buffer of various *PH* values. It was readily apparent that the heaviest precipitation occurred in tubes which were at PH 5.0 and 5 1, as was afterwards shown by testing with the quinhydrone electrode. Repetition of the experiment gave the same result. In a few instances the urease precipitate was centrifuged off and analyzed for its activity. The urease was found to be about 50% precipitated at PH 5.0 to 5.1. Below *PH* 4.8 and above *PH* 5 **3** no precipitate was produced. We were able also to precipitate urease by bubbling carbon dioxide through its solution. As nearly as could be found maximum precipitation by carbonic acid occurred at *PH* 5.0 to 5.1.

TABLE I

PRECIPITATION OF UREASE BY ACETATE BUFFER

Experiment 1		Experiment 2	
PH	Precipitate	*PH*	Precipitate
4.82	None	4.80	Faint
4.91	Moderate	4.88	Moderate
5.00	Heavy	4.98	Heavy
5.10	Heavy	5.10	Heavy
5.20	Moderate	5.18	Faint
5.30	Very faint	5.30	None

Accordingly we report the isoelectric point of crystalline urease as determined by the PH of minimum solubility to be at PH 5.0 to 5.1. The greatest possibility of error is dependent upon the purity of the urease employed. Our material is admitted not to be as pure as that which might have been prepared by several recrystallizations, starting with crystals obtained from jack bean meal of highest activity.

The isoelectric point is thus shown to be far to the acid side of the PH of optimum activity. We have previously found this for crystalline urease to be at *PH* 7.0. Urease is active on both sides of the isoelectric point with no sudden change in activity in passing from one side to the other. Indeed, the enzyme is still active in solutions as acid as PH **3.8,** although it is being steadily destroyed at this acidity.

Summary

1. Crystalline urease undergoes electrophoresis toward the anode in solutions of buffer varying from neutrality to about *PH* **5.5.** In buffer more acid than **5.5** no migration could be confirmed.

2. Urease begins to be precipitated by potassium acid phthalate at **PH 5.3** and the precipitation is almost complete at *PH* 4.6.

3. Urease begins to be precipitated by buffered lead acetate at *PH* 4.7 and the precipitation is almost complete at *PH* 5.6. The regions for precipitation by phthalate and lead overlap at *PH* 4.95, where 20% of the urease is precipitated by either ion. Urease is precipitated by mercuric and cupric ions over a much wider range than for lead ions.

4. Dilute electrolytes have three effects on the solubility of urease: ***a*** precipitation by certain ions such as phthalate and lead, over a certain range of PH; a solvent effect on urease; a precipitating action where the dilute salts bring the solution to the *PH* of the isoelectric point of urease.

5. The isoelectric point of urease as determined by the point of minimum solubility in dilute acetate buffer is at *PH* 5.0 to **5.1.** This point is far to the acid side of the *PH* of optimum activity for urease. Urease is active on both sides of its isoelectric point.

ITHACA, NEW YORK

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

THE PREPARATION OF CERTAIN OCTADECANOIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XV[1]

BY W. M. STANLEY,[2] MARIAN S. JAY[2] AND ROGER ADAMS

RECEIVED NOVEMBER 15, 1928 PUBLISHED APRIL 5, 1929

In previous papers numerous series of organic acids of the general formula $RCH(CO_2H)R'$ in which R is a cyclohexyl, cyclopentyl, cyclopentenyl, or cyclopropyl group, or in which R is one of these groups substituted in the ω-position of the alkyl group, and in which R' is an alkyl group, have been prepared and studied for their bactericidal action toward B. leprae. The results indicated that there are no very marked differences between the acids containing the 3, 5 or 6-membered rings, and consequently the supposition that a ring is an important factor for the bactericidal action is probably incorrect. The acids which gave the best results in each of the series studied were those containing from sixteen to eighteen carbon atoms. When the two substituted groups in the acetic acids were of approximately the same number of carbon atoms, the products in general had the most pronounced bactericidal action.

The object of the present investigation was to determine whether acids not containing a ring might have a bactericidal action. A number of isomeric octadecanoic acids were synthesized which included a complete series of compounds with a chain of seventeen carbon atoms and a carboxyl group substituted in every possible position. The bactericidal properties are reported in Table I.

The results indicate conclusively that no ring in the molecule is necessary for bactericidal action. The marked difference between the acid with the carboxyl at the end of the chain and those with the carboxyl at any other position is particularly to be noticed. The individual members of the series do not show as regular a variation in bactericidal properties with change in constitution as was found in the previous series containing the rings. In fact, the variability resembles to a certain extent that found in the previously prepared ring-containing acids which had nineteen

---

[1] For previous articles in this field see (a) Shriner and Adams, THIS JOURNAL, 47, 2727 (1925); (b) Noller with Adams, *ibid.*, 48, 1080 (1926); (c) Hiers with Adams, *ibid.*, 48, 1089 (1926); (d) 48, 2385 (1926); (e) Van Dyke and Adams, *ibid.*, 48, 2393 (1926); (f) Sacks with Adams, *ibid.*, 48, 2395 (1926); (g) Noller and Adams, *ibid.*, 48, 2444 (1926); (h) Adams, Stanley, Ford and Peterson, *ibid.*, 49, 2934 (1927); (i) Arvin with Adams, *ibid.*, 49, 2940 (1927); (j) Adams, Stanley and Stearns, *ibid.*, 50, 1475 (1928); (k) Yohe and Adams, *ibid.*, 50, 1503 (1928); (l) Arvin and Adams, *ibid.*, 50, 1983 (1928); (m) Davies and Adams, *ibid.*, 50, 2297 (1928).

[2] This communication is an abstract of portions of theses submitted by W. M. Stanley in partial fulfilment of the requirements for the degree of Doctor of Philosophy and by Marian S. Jay in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

TABLE I

BACTERICIDAL ACTION OF OCTADECANOIC ACIDS

	Dilutions of sodium salts in thousands											
	5	15	25	50	62	74	85	100	125	155	192	250
$C_{17}H_{35}CO_2H$	+	+	+	+	+	+	+	+	+	+	+	+
$CH_3CH(CO_2H)C_{15}H_{31}$	−	−	−	−	−	±	±	±	±	+	+	+
$C_2H_5CH(CO_2H)C_{14}H_{29}$	−	−	−	−	−	−	−	−	−	−	±	+
$C_3H_7CH(CO_2H)C_{13}H_{27}$	±	±	+	+	+	+	+	+	+	+	+	+
$C_4H_9CH(CO_2H)C_{12}H_{25}$	−	±	±	+	+	+	±	+	+	+	+	+
$C_5H_{11}CH(CO_2H)C_{11}H_{23}$	−	−	±	±	+	+	+	+	+	+	+	+
$C_6H_{13}CH(CO_2H)C_{10}H_{21}$	−	−	−	−	−	±	±	+	+	+	+	+
$C_7H_{15}CH(CO_2H)C_9H_{19}$	−	−	−	−	−	±	±	±	±	+	+	+
$C_8H_{17}CH(CO_2H)C_8H_{17}$	−	−	−	−	−	±	−	±	+	+	+	+
$(CH_3)_2CHCH(CO_2H)C_{13}H_{27}$	±	+	+	+	+	+	+	+	+	+	+	+
$(CH_3)_2CHCH_2CH(CO_2H)C_{12}H_{25}$	−	−	−	±	±	+	+	+	+	+	+	+
$C_2H_5CH(CH_3)CH(CO_2H)C_{12}H_{25}$	−	−	−	−	−	−	±	+	+	+	+	+
$C_3H_7CH(CH_3)CH(CO_2H)C_{11}H_{23}$	−	−	−	−	−	±	+	+	+	+	+	+

to twenty-one carbon atoms. It seemed probable, therefore, that analogous acids of somewhat lower molecular weight, such as hexadecanoic acids, should prove more effective. A complete series of acids was synthesized which contained a chain of fifteen carbon atoms with the carboxyl in each possible position. The bacteriological results are given in Table II.

TABLE II

BACTERICIDAL ACTION OF HEXADECANOIC ACIDS

	Dilutions of sodium salts in thousands											
	5	15	25	50	62	74	85	100	125	155	192	250
$C_{15}H_{31}CO_2H$	+	+	+	+	+	+	+	+	+	+	+	+
$CH_3CH(CO_2H)C_{13}H_{27}$	−	−	−	−	±	±	+	+	+	+	+	+
$C_2H_5CH(CO_2H)C_{12}H_{25}$	−	−	−	−	−	−	−	−	±	+	+	+
$C_3H_7CH(CO_2H)C_{11}H_{23}$	−	−	−	−	−	−	=	t i	+	+	+	+
$C_4H_9CH(CO_2H)C_{10}H_{21}$	−	−	−	−	−	−	−	−	−	±	±	+
$C_5H_{11}CH(CO_2H)C_9H_{19}$	−	−	−	−	−	−	−	±	±	+	+	+
$C_6H_{13}CH(CO_2H)C_8H_{17}$	−	−	−	−	−	−	−	−	−	−	−	+
$C_7H_{15}CH(CO_2H)C_7H_{15}$	−	−	−	−	−	−	−	−	−	−	±	+
$(CH_3)_2CHCH_2CH(CO_2H)C_{10}H_{21}$	−	−	−	−	−	−	−	−	−	−	±	±
$C_2H_5CH(CH_3)CH(CO_2H)C_{10}H_{21}$	−	−	−	−	−	−	−	±	+	+	+	+

Analysis of the data indicates that the prediction was correct. The acids were in practically every instance more bactericidal than the octadecanoic acid homologs. Moreover, the regularity in the change of bactericidal property with constitution, which did not exist in the acids of eighteen carbon atoms, is apparent here. The marked difference between the acid with the carboxyl at the end of the chain and acids with the carboxyl in any other position again deserves notice.

The conclusion from the studies of the bactericidal effect toward acid-fast bacteria, and especially toward B. *leprae*, of the large number of acids described in this series of papers, is that the effect can hardly be attributed to a chemical specificity of the individual acids but must, probably, be due to a combination of physical properties common to many of these acids. The mechanism of the bactericidal effect may be looked upon as an adsorption or solution of the acid in the waxy coating of the bacteria, with a consequent smothering or suffocation of the organism. The physical properties of the effective acids are being studied in an attempt to correlate physical properties and bactericidal action.

Although occasional tests have been made to determine the bactericidal effect of some of these acids toward B. *smegmatis* and *B. tuberculosis,* no report of the results has as yet been published. The relative bactericidal action for B. *tuberculosis* and *B. leprae* of a few selected acids is recorded in Table III.

TABLE III

BACTERIOLOGICAL ACTION OF CERTAIN ACIDS TO B. *tuberculosis*

	Dilution of sodium salts in thousands									Max **eff. diln.** *vs.* B. *leprae* in thousands
	1	5	10	16	20	25	33	50	100	
$C_7H_{15}CH(CO_2H)C_7H_{15}$	—	—	—	—	—	—	—	±	+	155
$C_6H_{11}(CH_2)_2CH(CO_2H)CH_2C_6H_{11}$	—	—	—	—	—	—	—	—	+	100
$C_6H_{11}(CH_2)_2CH(CO_2H)C_7H_{15}$	—	—	—	—	—	—	—	±	+	220
$C_6H_{11}CH(CO_2H)C_{10}H_{21}$	—	—	—	—	—	—	—	±	+	180
$C_5H_7(CH_2)_2CH(CO_2H)C_{10}H_{21}$	—	—	—	—	±	+	+	+	+	192
$C_6H_{11}(CH_2)_3CH(CO_2H)(CH_2)_3C_6H_{11}$	—	+								25
$C_6H_{11}(CH_2)_4CH(CO_2H)(CH_2)_2C_6H_{11}$	—	+								***25***

It is obvious that the acids are in general only a fraction as effective toward B. *tuberculosis* as they are toward B. *leprae;* nevertheless they do have a similar action. The acids of too high molecular weight have a relatively low effect just as was found in the tests against B. *leprae.*

TABLE IV

BACTERICIDAL TESTS TOWARD VARIOUS STRAINS OF B. *leprae*

	No. of strain	Dilution of sodium salts in thousands											
		10	25	50	75	100	120	142	160	182	200	221	250
Mixed acids of *Hydnocarpus Alcalae*	1	—	—	—	—	—	±	±	+	+	+	±	+
	2	—	—	—	±	—	±	+	+	+	+	+	+
	3	—	—	+	+	+	+	+	+	+	+	+	+
	4	—	—	—	—	±	±	—	—	—	—	+	+
	5	—	—	±	—	—	+	±	+	±	+	+	+
	6	—	—	+	+	+	+	+	+	+	+	-	*t i*
	7	—	±	+	+	+	+	±	+	+	+	+	+
	8	—	—	—	±	+	+	+	+	+	+	+	+
Mixed acids of Chaulmoogra Oil	1	—	—	—	—	—	—	±	+	+	+	+	+
	2	—	—	—	—	—	+	±	±	±	+	+	+
	3	—	—	—	—	—	±	+	+	+	+	+	+
	4	—	—	—	—	*	—	—	—	—	+	±	+
	5	—	—	—	—	—	—	—	±	+	+	+	+
	6	—	—	—	±	±	+	±	+	+	+	+	+
	7	—	—	—	±	±	+	+	+	+	+	+	+
	8	—	—	—	—	—	±	+	+	+	+	+	+

TABLE IV (*Concluded*)

	No. of strain	Dilution of sodium salts in thousands 10	25	50	75	100	120	142	160	182	200	221	250
	1	–		–	–	±	+	+	+	+	+	+	+
	2	–	–	–	–	+	+	+	+	+	+	+	+
	3	–		–	–	+	+	+	+	+	±	+	+
$C_5H_7CH(CO_2H)C_9H_{19}$	4	–		–	–	–	–	–	–	–	–	–	±
	5	–		–	–	–	–	–	* –	+	+	±	+
	6	–		±	+	+	+	+	+	+	+	+	+
	7	–		–	–	+	+	+	+	+	+	+	+
	8	–		–	–	+	+	+	+	+	+	+	+
	1	–	–	–	–	–	–	–	–	–	–	–	±
	2	–	–	–	–	–	–	–	–	–	±	±	±
	3	–	–	–	–	–	–	–	–	–	–	–	+
$C_5H_9(CH_2)_2CH(CO_2H)C_8H_{17}$	4	–	–	–	–	–	–	–	–	–	–	±	±
	5	–	–	–	–	–	–	–	–	–	±	+	+
	6	–	–	–	–	–	–	–	–	–	–	±	+
	7	–	–	–	–	–	–	–	–	–	±	±	+
	8	–	–	–	–	–	–	–	–	–	±	+	+
	1	–	–	–	–	–	–	–	–	–	–	–	±
	2	–	–	–	±	±	+	+	+	+	+	+	+
	3	–	–	–	–	–	–	–	–	–	–	±	±
$C_6H_{11}(CH_2)_2CH(CO_2H)C_8H_{17}$	4	–	–	–	–	–	–	–	–	–	–	–	–
	5	–	–	–	–	–	–	–	–	–	–	–	+
	6	–	–	–	–	–	–	–	–	–	–	±	+
	7	–	–	–	–	–	–	–	–	–	–	±	±
	8	–	–	–	–	–	–	–	–	±	+	+	+

Strain 1 is a culture of B. leprae of unknown history obtained from the University of Chicago. It has been cultured on laboratory media for several years and is a very rapidly-growing strain. All of the tests made on the various acids have been with this particular organism. Strains 2 to 8 inclusive were obtained from the American Type Culture Collection and are listed as follows: No. 2, 65 Hyg. Lab., Washington, D. C., 365—"Duval," 1925; No. 3, 66 Hyg. Lab., Washington, D. C., 367—"rat 2," 1925; No. 4, 67 Hyg. Lab., Washington, D. C., 368—"rat 12, Dr. McCoy," 1925; No. 5, 68 Hyg. Lab., Washington, D. C., 361—"Needham," 1925; No. 6, 69 Army Med. School, Washington, D. C., 366—"rat 1," 1925; No. 7, 282 of American Type Culture Collection; No. 8, 283 of American Type Culture Collection.

In order to be certain that the acids are bactericidal toward strains of B. leprae other than that regularly used, a few tests were made and are recorded in Table IV. Three synthetic acids and the mixed acids from two natural oils were studied, using eight different strains of bacteria.

It can be seen that the synthetic acids are much more bactericidal than the mixed acids of the natural oils, and that the results run parallel with the different, more or less resistant, strains. Strain 4 is obviously much more easily killed than the others and too much significance should, therefore, not be attached to the results on this particular one.

The synthetic acids were prepared from the proper disubstituted malonic esters by saponification and decomposition of the malonic acids.

Experimental

The general methods of preparation of the various intermediates have been described in previous articles in this series.

TABLE V

DIETHYL DIALKYL MALONATES (INTERMEDIATES FOR C_{18} ACIDS)

	B. p., °C.	n_D^{25}	d_4^{25}	Found,[a] %	
$CH_3C(CO_2C_2H_5)_2C_{15}H_{31}$	179–183 (5 mm.)	1.4453	0.9119	71.71	11.38
$C_2H_5C(CO_2C_2H_5)_2C_{14}H_{29}$	172–177 (3 mm.)	1.4461	.9163	71.67	11.52
$C_3H_7C(CO_2C_2H_5)_2C_{13}H_{27}$	183–187 (5 mm.)	1.4475	.9048	71.66	11.36
$C_4H_9C(CO_2C_2H_5)_2C_{12}H_{25}$	175–180 (3.5 mm.)	1.4473	.9104	71.48	11.33
$C_5H_{11}C(CO_2C_2H_5)_2C_{11}H_{23}$	180–185 (5 mm.)	1.4509	.9124	72.01	11.32
$C_6H_{13}C(CO_2H_5)_2C_{10}H_{21}$	185–188 (2.5 mm.)	1.4476	.9118	71.27	11.40
$C_7H_{15}C(CO_2C_2H_5)_2C_9H_{19}$	193–197 (5 mm.)	1.4471	.9118	71.59	11.47
$C_8H_{17}C(CO_2C_2H_5)_2C_8H_{17}$	192–195 (3 mm.)	1.4471	.9135	71.35	11.58
$(CH_3)_2CHC(CO_2C_2H_5)_2C_{13}H_{27}$	179–183 (5 mm.)	1.4491	.9144	71.59	11.38
$(CH_3)_2CHCH_2C(CO_2C_2H_5)_2C_{12}H_{25}$	180–185 (5 mm.)	1.4481	.9115	71.51	11.74
$C_2H_5CH(CH_3)C(CO_2C_2H_5)_2C_{12}H_{25}$	180–184 (5 mm.)	1.4501	.9163	72.01	11.31
$C_3H_7CH(CH_3)C(CO_2C_2H_5)_2C_{11}H_{23}$	175–178 (4 mm.)	1.4509	.9155	71.73	11.34

[a] Calcd. for $C_{23}H_{44}O_4$: C, 71.81; H, 11.54.

TABLE VI

DIETHYL DIALKYL MALONATES (INTERMEDIATES FOR C_{16} ACIDS)

	B. p., °C.	n_D^{25}	d_4^{25}	Found,[a] % C	H
$CH_3C(CO_2C_2H_5)_2C_{13}H_{27}$	167–170 (3 mm.)	1.4418	0.9181	70.48	11.16
$C_2H_5C(CO_2C_2H_5)_2C_{12}H_{25}$	181–183 (4 mm.)	1.4422	.9249	70.40	11.29
$C_3H_7C(CO_2C_2H_5)_2C_{11}H_{23}$	178–179 (4 mm.)	1.4422	.9186	70.50	11.22
$C_4H_9C(CO_2C_2H_5)_2C_{10}H_{21}$	181–183 (4 mm.)	1.4424	.9220	70.81	11.20
$C_5H_{11}C(CO_2C_2H_5)_2C_9H_{19}$	185–186 (5 mm.)	1.4462	.9282	70.45	11.00
$C_6H_{13}C(CO_2C_2H_5)_2C_8H_{17}$	175–178 (4 mm.)	1.4458	.9168	70.38	11.18
$C_7H_{15}C(CO_2C_2H_5)_2C_7H_{15}$	178–180 (3 mm.)	1.4459	.9169	70.50	11.20
$(CH_3)_2CHCH_2C(CO_2C_2H_5)_2C_{10}H_{21}$	160–162 (2 mm.)	1.4428	.9207	70.51	11.00
$C_2H_5CH(CH_3)C(CO_2C_2H_5)_2C_{10}H_{21}$	196–198 (10 mm.)	1.4454	.9253	70.70	11.01

[a] Calcd. for $C_{21}H_{40}O_4$: C, 70.78; H, 11.24.

TABLE VII

OCTADECANOIC ACIDS

	M. p., °C.	B. p., °C.	n_D^{25}	d_4^{25}	Found,[a] % C	H
$CH_3CH(CO_2H)C_{15}H_{31}$[b]	34–35	179–183 (5 mm.)	....	....	76.20	12.54
$C_2H_5CH(CO_2H)C_{14}H_{29}$	23–24	167–170 (2.5 mm.)	1.4531	0.8767	76.03	12.55
$C_3H_7CH(CO_2H)C_{13}H_{27}$	31–32	179–183 (5 mm.)	...	....	75.90	12.46
$C_4H_9CH(CO_2H)C_{12}H_{25}$	23–24	180–184 (4 mm.)	1.4528	.8743	76.03	12.54
$C_5H_{11}CH(CO_2H)C_{11}H_{23}$	...	180–185 (4 mm.)	1.4519	.8829	76.21	12.48
$C_6H_{13}CH(CO_2H)C_{10}H_{21}$[c]	...	182–184 (5 mm.)	1.4527	.8741	75.79	12.73
$C_7H_{15}CH(CO_2H)C_9H_{19}$[c]	...	180–183 (5 mm.)	1.4528	.8747	75.92	12.83
$C_8H_{17}CH(CO_2H)C_8H_{17}$[d]	35–36	183–185 (5 mm.)	....	....	76.00	12.75
$(CH_3)_2CHCH(CO_2H)$-$C_{13}H_{27}$	58–59	178–182 (5 mm.)	....		76.11	12.51

TABLE VII (Concluded)

	M. p., °C.	B. p., °C.	n_D^{25}	d_4^{25}	Found,[a] % C	H
$(CH_3)_2CHCH_2CH(CO_2H)$-$C_{12}H_{25}$	26–27	175–180 (4 mm.)	....	....	76.02	12.52
$C_2H_5CH(CH_3)CH(CO_2H)$-$C_{12}H_{25}$	38–39	178–183 (6 mm.)	....	. .	75.82	12.56
$C_3H_7CH(CH_3)CH(CO_2H)$-$C_{11}H_{23}$	37–38	175–178 (5 mm.)	....	....	76.24	12.58

[a] Calcd. for $C_{18}H_{36}O_2$: C, 75.98; H, 12.76.

[b] This acid has been previously described and is reported as having m. p. 51–51.5° [Morgan and Holmes, J. *Soc. Chem.* Ind., **46,** 152 (1927)].

[c] These acids and the necessary intermediates were prepared by Gerald H. Coleman.

[d] This acid has been previously described and is reported as having m. p. 38.5°, b. p. 270–275 (100 mm) [M. Guthzeit, Ann., **204,** 11 (1880)].

TABLE VIII

HEXADECANOIC ACIDS

	B. p , °C.	M. p , °C.	n_D^{25}	d_4^{25}	Found,[a] % C	H
$CH_3CH(CO_2H)C_{13}H_{27}$[b]	172–173 (2.5 mm)	24	1.4453	0.8765	74.74	12.48
$C_2H_5CH(CO_2H)C_{12}H_{25}$	178–179 (3 mm.)	23	1.4460	.8808	75.20	12.50
$C_3H_7CH(CO_2H)C_{11}H_{23}$	178–179 (3 mm.)	16.5–17	1.4460	.8808	74.65	12.49
$C_4H_9CH(CO_2H)C_{10}H_{21}$	175–176 (3 mm.)	13–14	1.4458	.8789	74.60	12.42
$C_5H_{11}CH(CO_2H)C_9H_{19}$	178–179 (3 mm.)	9–10	1.4518	.8887	74.90	12.30
$C_6H_{13}CH(CO_2H)C_8H_{17}$[c]	165–168 (2 mm.)	.....	1.4495	.8768	74.82	12.56
$C_7H_{15}CH(CO_2H)C_7H_{15}$[c,d]	187–189 (4 mm.)	26–27	1.4497	.8771	74.72	12.56
$(CH_3)_2CHCH_2CH$-$(CO_2H)C_{10}H_{21}$	187–188 (9 mm.)	17.5–18	1.4448	.8763	75.30	12.70
$C_2H_5CH(CH_3)CH$-$(CO_2H)C_{10}H_{21}$	185–186 (9 mm.)	38–39	. . .	....	74.72	12.56

[a] Calcd. for $C_{16}H_{32}O_2$: C, 75.00; H, 12.70.

[b] This acid has been previously described and is reported as having m. p. 48° [Morgan and Holmes, J. *Soc. Chem. Ind.*, **46,** 152 (1927)].

[c] These acids and the necessary intermediates were prepared by Gerald H. Coleman.

[d] This acid has been previously described and is reported as having m. p. 26–27°, b. p. 240–250° (85 mm.) [F. Jourdan, *Ann.* **200,** 116 (1880)].

Summary

1. It has been demonstrated that *a* ring structure is unnecessary in order that certain various organic acids have a bactericidal action.

2. A number of octadecanoic acids and hexadecanoic acids have been synthesized and their bactericidal actions determined.

3. A table of bactericidal values toward B. *tuberculosis* of a few selected acids is included. The effect is much less than toward B. *leprae.*

4. A table of bactericidal values of a few acids toward eight different strains of B. *leprae* is given.

URBANA, ILLINOIS

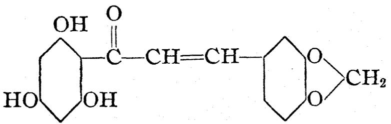
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

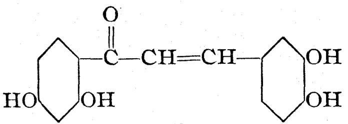
SYNTHESIS OF SOME CHALKONES

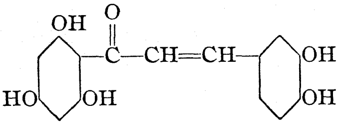
BY R. L. SHRINER AND E. C. KLEIDERER

RECEIVED NOVEMBER 19, 1928 PUBLISHED APRIL 5, 1929

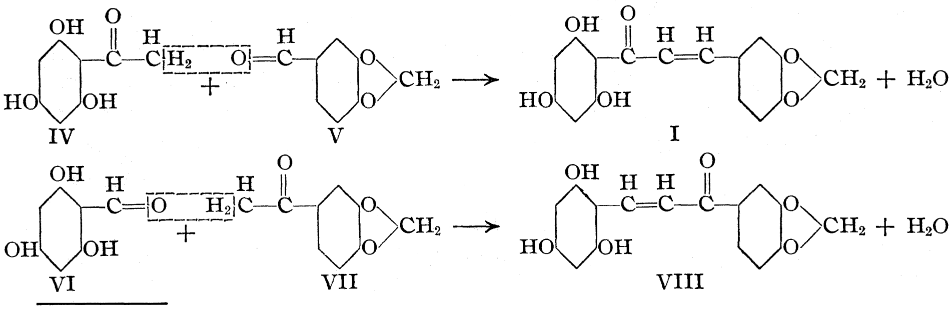
A yellow coloring matter, hyssopin, first isolated from *Herba Hyssopi* by Tunmann,[1] was shown to be a rhamnoside of a chaikone by Oesterie and Kueny.[2] Oesterle[3] also prepared it from *Capsella Bursa Pastoris* and studied its decomposition by 33% potassium hydroxide. Since piperonal, acetopiperone and phloroglucinol were obtained by this alkaline degradation, Oesterle decided that the chalkone was 2,4,6-trihydroxyphenyl-3,4-methylenedioxystyryl ketone (I). This structure was analogous to that assigned to butein (II) by Perkin and Hummel,[4] and Göschke and Tambor,[5] who have synthesized the latter compound. It is also similar to the structure given to eriodictyol (III) by Tutin.[6]


I


II


III

However, since only a small amount of piperonal was obtained and acetopiperone predominated among the decomposition products, it would seem that the chalkone should be 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone (VIII). The purpose of the present investigation was to synthesize the two isomeric chalkones represented by Formulas (I) and (VIII).



---

[1] Tunmann, *Pharm. Post.*, 90,773 (1917).

[2] Oesterle and Kueny, *Schweiz. Apoth.-Ztg.*, 59, 548 (1921).

[3] Oesterle, *ibid.*, 60, 441 (1922).

[4] Perkin and Hummel, J. *Chem. Soc.*, *85*, 1459 (1904).

[5] Göschke and Tambor, Ber., 44,3502 (1911).

[6] Tutin, J. *Chem. Soc.*, 97,2054,2062 *(1910)*.

The first isomer (I) was prepared by condensing 2,4,6-trihydroxyacetophenone (IV) with piperonal (V) by means of alcoholic potassium hydroxide. The 2,4,6-trihydroxyacetophenone was made by condensing phloroglucinol with acetyl chloride by means of aluminum chloride in nitrobenzene as a solvent.'

The second isomer (VIII) was synthesized by the condensation of phloroglucinaldehyde (VI) with acetopiperone (VII). The phloroglucinaldehyde was prepared by means of the Gattermann reaction using the modified procedure of Adams and Levine.[8] Dry hydrogen chloride was passed into a suspension of zinc cyanide in an ether solution of phloroglucinol. The resulting imidohydrochloride was then hydrolyzed to phloroglucinaldehyde. Acetopiperone was prepared by the ketonic hydrolysis of piperonyl acetic ester[S] obtained by condensing methyl piperonylate with ethyl acetate by the use of sodium. The chalkone was obtained by condensing together the above aldehyde (VI) and ketone (VII) with alcoholic alkali.

These chalkones decompose on heating and do not possess definite melting points. Their acetates, however, melt sharply and hence the triacetate of each of the isomers was prepared. The natural product decomposed at 262–263° and its triacetate melted at 196–197° according to Oesterle.[3] The synthetic chalkone corresponding to Formula (I) decomposed above 300° and yielded an acetyl derivative melting at 218–220°. Compound VIII decomposed at 265–270° and yielded an acetate melting at 205–206°. It will be noted that the synthetic chalkone (VIII) decomposed at very nearly the same temperature as the natural product. It also possessed properties which agreed with those given by Oesterle for his compound, but the triacetate of this synthetic chalkone melted ten degrees higher than the acetate prepared from the natural substance. Since it is very difficult to purify these natural coloring matters it may be that the natural product was not quite pure. It is very evident that chalkone I diiers markedly from the natural product. Its decomposition point and the melting point of its triacetate are very much higher than the values for the natural chalkone. Unfortunately, no sample of the natural product could be obtained for direct comparison.

Experimental

Piperonal.—The piperonal was a commercial product and was purified by vacuum distillation. It melted at 36°.

2,4,6-Trihydroxyacetophenone.—Fifteen grams of phloroglucinol and 20 g. of acetyl chloride were dissolved in a mixture of 200 cc. of dry nitrobenzene and 200 cc. of absolute ether. Thirty grams of aluminum chloride was then added in small portions

---

[7] Rosenmund and Schulz, *Arch. Pharm.*, **265**, 318 (1927).

[8] Adams and Levine, This Journal, **45**, 2373 (1923).

[9] Mauthner, *J. prakt. Chem.*, **116**, 321 (1917).

during a period of half an hour. The ether was distilled and an additional 30 g. of aluminum chloride was added to the solution. which was stirred vigorously and allowed to stand overnight. The mass was decomposed with ice and the nitrobenzene removed by steam distillation. The aqueous residue was filtered while still hot. On cooling the filtrate, trihydroxyacetophenone crystallized out. After two crystallizations from water with the aid of Norite, 5 g. of light yellow needles was obtained which melted at 213–214° (corr.). The compound gave a wine-red color with ferric chloride, which differentiates it from phloroglucinol, which melts at 217–218°.

Anal. Subs., 0.1341: H_2O, 0.0563; CO_2, 0.2819. Calcd. for $C_8H_8O_4$: H, 4.76; C, 57.14. Found: H, 4.69; C, 57.33.

2,4,6-Trihydroxyphenyl-3,4-methylenedioxystyryl Ketone (I).—This chalkone was obtained by mixing together 2 g. of piperonal, 2 g. of chloro-acetophenone and 20 cc. of 50% alcohol in which 5 g. of potassium hydroxide had been dissolved. The mixture was heated for one hour at 95–100°. After cooling, it was poured into dilute hydrochloric acid and the yellow precipitate filtered off. After recrystallization from 75% methyl alcohol, a yellow powder was obtained which decomposed around 300–310°.

Anal. Subs., 0.0986: H_2O, 0.0365; CO_2, 0.2309. Calcd. for $C_{16}H_{12}O_6$: H, 4.03 C, 64.00. Found: H, 4.13; C, 63.85.

The acetate was prepared by refluxing 1 g. of the above chalkone with 15 cc. of acetic anhydride and 1 g. of anhydrous sodium acetate for one hour. On pouring into water the acetate separated as a light yellow solid. It was recrystallized from 90% alcohol and consisted of light yellow needles melting at 218–220°.

Anal. Subs., 0.1071: H_2O, 0.0386; CO_2, 0.2419. Calcd. for $C_{22}H_{18}O_9$: H, 4.22; C, 61.97. Found: H, 4.03; C, 61.56.

Phloroglucinaldehyde.—Dry hydrogen chloride was passed into a mixture of 30 g. of phloroglucinol dissolved in 250 cc. of dry ether with 30 g. of zinc cyanide with vigorous mechanical stirring. At the end of two hours the imido-hydrochloride separated as an oil. The supernatant liquid was decanted and the crude imido-hydrochloride washed with ether. The product then solidified. It was boiled with 250 cc. of water for three minutes and the solution cooled. Orange-red crystals of the crude aldehyde separated and were purified by two crystallizations from hot water in the presence of Norite. Long, white needles were obtained which possessed no definite melting point. This compound gave a wine-red color with ferric chloride and yielded a phenylhydrazone melting at 120°; yield 18 g. or 49% of the theoretical.

Anal. Subs., 0.1268: H_2O, 0.0451; CO_2, 0.2521. Calcd. for $C_7H_6O_4$: H, 3.89; C, 54.50. Found: H, 3.98; C, 54.28.

Acetopiperone.—A mixture of 24 g. of methyl piperonylate, 3.1 g. of powdered sodium and 18 g. of ethyl acetate was heated on the steam-bath for two hours. At the end of this time an additional 2 g. of sodium and 10 g. of ethyl acetate were added and the heating was continued for another two hours, at which time 10 g. of ethyl acetate was again added and the heating allowed to continue for four hours. The addition of the ethyl acetate in this manner is necessary in order to get the methyl piperonylate to condense, since a considerable portion of the ethyl acetate condenses with itself to give ethyl acetoacetate.

The reaction mixture was decomposed with water and acidified with acetic acid. The oil which separated was crude 3,4-methylenedioxybenzoylacetic ester. This was washed with water and then hydrolyzed by refluxing with 300 cc. of 10% sulfuric acid for eight hours. After cooling, the solution was made alkaline with sodium hydroxide and extracted with ether. The ether was distilled and the acetopiperone recrystallized from 50% alcohol. Eight grams of white crystals was obtained which melted at 87–88°.

The compound yielded a *p*-nitrophenylhydrazone melting at 201–203°, which agrees with the value given by Mauthner.[9]

Anal. Subs., 0.1011: H_2O, 0.0457; CO_2, 0.2424. Calcd. for $C_9H_8O_3$: H, 4.88; C, 65.90. Found: H, 5.05; C, 65.45.

2,4,6-Trihydroxystyryl-3,4-methylenedioxyphenyl **Ketone** (VIII).—Two grams of phloroglucinaldehyde and 2 g. of acetopiperone were condensed by the method described above for the other isomer. Crystallization from 75% methyl alcohol yielded an orange powder which decomposed at 265–270°. In its decomposition point, color (deep orange) and also its insolubility in dilute ammonia, this compound resembled the natural product described by Oesterle.

Anal. Subs., 0.0770; H_2O, 0.0289; CO_2, 0.1798. Calcd. for $C_{16}H_{12}O_6$: H, 4.03; C, 64.00. Found: H, 4.20; C, 63.71.

The triacetate was prepared by refluxing 1 g. of the above ketone with acetic anhydride and sodium acetate for one hour. After decomposition with and crystallization from alcohol, light yellow needles were obtained which melted at 205–206°.

Anal. Subs. 0.0876: H_2O, 0.0328; CO_2, 0.1995. Calcd. for $C_{22}H_{18}O_9$: H, 4.22; C, 61.97. Found: H, 4.18; C, 62.08.

Summary

The two isomeric chalkones, 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone and 2,4,6-trihydroxyphenyl-3,4-methylenedioxystyryl ketone, corresponding to the possible structures for the chalkone previously isolated from natural sources, have been synthesized. A comparison of the properties of the natural chalkone with those of the synthetic isomers indicates that the natural compound is 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone. The other isomer, which possesses the structure originally assigned to the natural chalkone, differs markedly from the compound found in nature.

URBANA, ILLINOIS

[CONTRIBUTED FROM THE CHEMICAL ENGINEERING LABORATORY, IOWA STATE COLLEGE]

DIFURYLETHYLENE

BY PAUL F. BRUINS

RECEIVED NOVEMBER 19, 1928 PUBLISHED APRIL 5, 1929

In making a study of the disappearance of furfural in alcohol fermentation, Lintner[1] found that furfural in dilute aqueous solution reacts with hydrogen sulfide to form a milky emulsion of polythiofurfuraldehyde which has a peculiar penetrating bread-like odor. The emulsion which was formed could be coagulated to a rubbery mass on the addition of a few drops of sulfuric or hydrochloric acid.

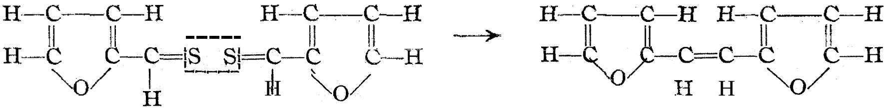
A study of this reaction has been made and an attempt to identify the product has brought about the discovery of a method whereby difurylethylene may easily be prepared. By the vacuum distillation of

---

[1] Lintner, Z. ges. *Brauw.*, 15,189 (1910); C. *A.*, 5,755 (1911).

the polythiofurfuraldehyde, difurylethylene is formed and is obtained almost pure in the distillate.

The mechanism of the reaction is probably of the following order:



The product of this reaction is one which should be of considerable value in the synthesis of furfural compounds. With the remarkable increase in the production of furfural and its accompanying low cost per pound, the synthesis of compounds made from furfural becomes increasingly interesting.

Experimental

The polythiofurfuraldehyde was prepared as follows: A 3% solution of furfural in water was placed in a large absorption bottle of about 4-liters capacity. A slow stream of hydrogen sulfide gas was passed through the solution for three hours. By raising the temperature of the solution to 50°, the absorption rate may be increased. The resulting emulsion was coagulated with a small amount of hydrochloric acid and the resulting mass dried as much as possible without warming.

One hundred grams of the polythiofurfuraldehyde was placed in a 500-cc. Claisen flask and slowly warmed with a low flame, maintaining a vacuum of from 10 to 15 mm. of mercury. At about 60° a slight amount of ebullition took place but the solid crystals did not begin to condense on the walls of the receiver until 90". The distillation was complete at 135°, leaving only a char. The product had a small amount of water with it and had a very penetrating odor due to a trace of sulfur compounds. The odor was entirely removed by petroleum ether, in which the compound which was formed was only slightly soluble.

The compound was purified by redistillation in *vacuo*. It was found that recrystallization from alcohol caused the compound to darken, indicating its rather unstable structure. It did not discolor farther on standing and the redistilled compound remained white. The yield was 18 g., or 18%.

Anal. Subs., 0.2076: CO_2, 0.5674; H_2O, 0.0960. Calcd. for C_5H_4O: C, 74.94; H, 5.09. Found: C, 74.55; H, 5.17.

The molecular weight determination using the freezing-point method with benzene as solvent was 162. The nearest theoretical weight would be 160.18, making the molecular formula $C_{10}H_8O_2$.

The compound melts at 100°. It is very soluble in acetone, soluble in benzene, ether, carbon tetrachloride, chloroform and hot alcohol, slightly soluble in petroleum ether and cold alcohol.

Summary

The vacuum distillation of polythiofurfuraldehyde, a compound prepared from furfural by treatment with hydrogen sulfide in dilute aqueous solution, yields what is believed to be difurylethylene.

AMES, IOWA

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

IDENTIFICATION OF AMINES. IV. METHANESULFONAMIDES

BY C. S. MARVEL, M. D. HELFRICK AND J. P. BELSLEY

RECEIVED NOVEMBER 21, 1928 PUBLISHED APRIL 5, 1929

The arylsulfonyl derivatives of primary and secondary amines have been carefully investigated and are very useful in the separation and identification of amines. However, very little work has been done on the alkylsulfonyl derivatives of this type. The work of Johnson and Ambler[1] shows that benzylsulfonamides are more easily hydrolyzed than are arylsulfonamides. It was thought that the simple alkylsulfonamides might hydrolyze even more readily than the benzyl derivatives and since ease of hydrolysis is a desirable property in sulfonamides if they are to be of value in the separation of amines, some of the methanesulfonamides were prepared and characterized.

Methanesulfonyl chloride has been prepared by the action of phosphorus pentachloride on methanesulfonic acid.[2] In this work the mixture of sodium methanesulfonate and sodium methyl sulfate obtained by the action of dimethyl sulfate on sodium sulfite was dried and treated directly with phosphorus pentachloride.

The methanesulfonamides could be prepared by the usual procedure using the sulfonyl chloride, the amine and aqueous alkalies. However, methanesulfonyl chloride is fairly easily hydrolyzed by water and the best yields of sulfonamides were obtained by working in benzene solutions. The methanesulfonamides were readily hydrolyzed by boiling them with 60% sulfuric acid for six hours.

Methanesulfonyl chloride has certain disadvantages as a reagent for the separation of amines. When an unknown mixture of primary, secondary and tertiary amines was treated with an excess of the reagent in the presence of cold aqueous alkalies, the primary amine was converted quite largely to the disulfonyl compound, which precipitated with the derivative of the secondary amine. Unless an excess of the reagent was used the tertiary amine was always contaminated with unchanged primary and secondary amine. When a known mixture of amines was treated with a known excess of the reagent, the amines were separated satisfactorily and the primary and secondary amines were recovered by hydrolysis of the derivatives.

Experimental Part

Methanesulfonyl Chloride.—In a 5-liter three-necked flask fitted with a reflux condenser, mechanical stirrer and a separatory funnel, were placed 1 kg. of anhydrous sodium sulfite and 2 liters of hot water (80–90°). The mixture was stirred and heated

---

[1] Johnson and Ambler, THIS JOURNAL, 36, 385 (1914).

[2] Carius, *Ann.*, 114, 142 (1860).

on the steam cone for about ten minutes to get as much in solution as was possible. The heating was discontinued and then 1 kg. of dimethyl sulfate was added at such a rate that the solution boiled gently. When all of the dimethyl sulfate had been added, the condenser was set for distillation and the water was distilled off under reduced pressure until a pasty mass just fluid enough to pour remained in the flask. This mixture was transferred to a large porcelain dish and dried in an oven at 120° until the mass was solid. This mass was then ground in a mortar and dried again far about six hours at 120°. The powdered mixture of sodium methanesulfonate and sodium methyl sulfate was transferred to a 5-liter flask and mixed thoroughly with 1.4 kg. of phosphorus pentachloride. About 2 liters of dry benzene was added to give better contact between the two reacting substances. This mixture was heated to gentle boiling under a reflux condenser for ten to twelve hours. The reaction mixture was cooled and filtered with suction. The salt cake was washed with 500 cc. of dry benzene. The benzene solution was then carefully fractionated using a good column. The yield of methanesulfonyl chloride boiling at 158–162° was 200–250 g. (21–27% of the theoretical amount based on the sodium sulfite).

Methanesulfonamides.—For the preparation of the pure amide it was found that the best results were obtained by treating a benzene solution of two molecular proportions of the amine with a benzene solution of one molecular proportion of methanesulfonyl chloride. The amine hydrochloride was filtered off, the benzene evaporated and the sulfonamide recrystallized from dilute alcohol until it had a constant melting point. The results of these experiments are given in Table I.

TABLE I

METHANESULFONAMIDES

Amine	M. p. of amide, °C.	Amine	M. p. of amide, °C.
Aniline[a]	100.5	2,5-Dichloro-aniline	174
o-Toluidine	103	α-Naphthylamine	125.5
p-Toluidine	102.5	β-Naphthylamine	153.5
o-Anisidine	115.5	6-Phenoxybutylamine	79.5
p-Anisidine	116	Methylaniline	76.5
p-Phenetidine	125	Ethylaniline	59
o-Chloro-aniline	90.5	n-Propylaniline	76
p-Chloro-aniline	148	n-Butylaniline	73
p-Bromo-aniline	136	Benzylaniline	122

[a] McGowan, J. prakt. Chem., [2] 30, 282 (1884), prepared this amide but does not list its properties; Duguet, Chem. *Zentr.*, [1] 854 (1902), gives 99° as the melting point of this compound.

The derivatives of N-ethyl-p-toluidine, N-ethyl-o-toluidine, l-menthylamine, *sec.* butylaniline, diethylamine, di-n-butylamine and di-n-propylamine were oils. Satisfactory nitrogen analyses were obtained on the solid compounds. The derivatives of the primary amines were soluble in 10% aqueous sodium hydroxide.

Hydrolysis of Methanesulfonamides.—A suspension of 9.3 g. of methanesulfone-N-methylanilide in a solution of 30 cc. of concentrated sulfuric acid (sp. gr. 1.84) in 30 cc. of water was boiled under a reflux condenser for about six hours. The solution was made alkaline and distilled with steam. The distillate was extracted with ether and the ether evaporated. The residual oil weighed 3.8 g. (about 71% of the theoretical amount) and was shown to be methylaniline.

The oily methanesulfonyl derivative prepared from 17 g. of di-*n*-butylamine was hydrolyzed by boiling under reflux for six hours with a solution of 30 cc. of concentrated sulfuric acid in 30 cc. of water. The solution was then made alkaline and extracted with ether. The ether was extracted with aqueous hydrochloric acid. This solution was then evaporated to dryness. The yield of di-n-butylamine hydrochloride was 7.8 g.

Separation of Amine Mixtures.—A mixture of 10 g. of aniline, 10 g. of methylaniline, and 10 g. of dimethylaniline was suspended in a 10% excess of cold 10% aqueous sodium hydroxide. To the cold suspension 27 g. (about 20% excess) of methanesulfonyl chloride was added during about ten minutes. The temperature was never above 25° and was usually about 10–15". When the methanesulfonyl chloride had reacted, the solution was extracted with ether. The ether was evaporated and this residue was again treated with methanesulfonyl chloride and aqueous alkali as before.

After the second treatment the derivative of the primary amine was obtained by acidifying the combined alkaline solutions. The yield was 10.2 g. (55% of the theoretical amount). The unchanged tertiary amine was extracted from the ether solution with hydrochloric acid and the ether was then evaporated. The residue weighed 10.5 g. (60% of the theoretical amount) and was the pure secondary amine derivative. The tertiary amine was recovered to the extent of about 95% from the acid solution.

When the composition of the amine mixture was not known the results were never as satisfactory as those described above. Prolonged action of the sulfonyl chloride converted the primary amines to alkali-insoluble derivatives. These are undoubtedly the disulfonyl derivatives although they were not isolated and characterized.

Summary

Several methanesulfonamides have been prepared and characterized. They make suitable derivatives for many amines and they are more readily hydrolyzed than most sulfonamides. Some difficulties are encountered when methanesulfonyl chloride is used as a reagent for the separation of unknown amine mixtures.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CVI. LEUCO BASES OF A NEW CLASS OF DYESTUFFS CONTAINING PYRIMIDINE RINGS

BY TREAT B. JOHNSON

RECEIVED NOVEMBER 23, 1928 PUBLISHED APRIL 5, 1929

Certain representatives of the aniline dyes hold a place of great importance in the chemotherapy of bacterial diseases, and their practical use for the disinfection of tissues has received increased attention during recent years.[1] Some of these combinations, especially members of the triphenylmethane series, are highly bactericidal. Gentian violet and magenta, for example, have been shown to be able to inhibit growth of staphylococci and streptococci in culture media in dilutions as high as 1:100,000 to 1:1,000,000. It is important also to note that several of these dyestuffs

---

[1] J. W. Churchman, *J. Am. Med. Assocn.*, **79**, 1657 (1922); *Chim. industrie,* 10,212 (1923); *Stain Tech.,* **1**, **27**, 103 (1926); *Ind. Eng. Chem., 18,* 1322 (1926).

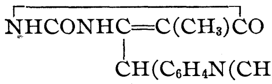
exhibit a remarkable variation in activity toward different bacterial organisms, a property which bears a close relationship to chemotherapy.

Notwithstanding the scientific interest that has been created in these compounds[2] and the increased attention that they have received by clinicians and bacteriologists, we have at present very little information regarding the relation of chemical constitution to their bactericidal and bacteriostatic properties, and also regarding the mechanism of their bactericidal activities. As a preliminary undertaking in the development of a new program of research on germicides the writer investigated, (with his co-workers) some new condensation reactions of certain pyrimidine aldehydes. The reactions reported at this time serve to illustrate the condensation possibilities of three typical pyrimidine aldehydes with aromatic bases under experimental conditions favoring the formation of leuco bases in the triphenylmethane series. The aldehydes thus far studied are derivatives of thymine as represented by Formulas I, II and III, respectively.

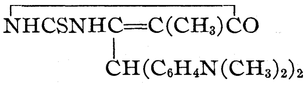
I $\overline{\text{NHCONHC(CHO)=C(CH}_3\text{)CO}}$ II $\overline{\text{NHCSNHC(CHO)=C(CH}_3\text{)CO}}$

III $\overline{\text{NHC(SC}_2\text{H}_5\text{)=NC(CHO)=C(CH}_3\text{)CO}}$

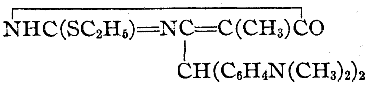
These aldehydes all condense smoothly with dimethylaniline in the presence of zinc chloride, giving the corresponding leuco compounds represented by Formulas IV, V and VI, respectively. These combinations

IV


$$\begin{array}{l}\overline{\text{NHCONHC=C(CH}_3\text{)CO}}\\ \qquad\qquad\quad |\\ \qquad\qquad\quad \text{CH(C}_6\text{H}_4\text{N(CH}_3)_2)_2\end{array}$$

V


$$\begin{array}{l}\overline{\text{NHCSNHC=C(CH}_3\text{)CO}}\\ \qquad\qquad\quad |\\ \qquad\qquad\quad \text{CH(C}_6\text{H}_4\text{N(CH}_3)_2)_2\end{array}$$

VI


$$\begin{array}{l}\overline{\text{NHC(SC}_2\text{H}_5\text{)=NC=C(CH}_3\text{)CO}}\\ \qquad\qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\qquad\quad \text{CH(C}_6\text{H}_4\text{N(CH}_3)_2)_2\end{array}$$

are leuco pyrimidine–malachite greens in which one benzene cycle of leuco malachite green has been replaced by a pyrimidine ring. All three of these leuco compounds are colorless substances and undergo oxidation in acid solution, giving soluble dyestuffs which dye silk fiber with beautiful effects. It is our belief that a program of research involving the study of these combinations can be organized which will aid in advancing our present knowledge of the chemotherapy of dyestuffs. Structural changes can be incorporated easily in the pyrimidine cycle, which will enable us to synthesize new dyestuffs in an orderly manner.

Experimental Part

p-2-Tetramethyldiaminodiphenyl-2-thiothyminylmethane, V.—In order to prepare this leuco compound we used the following reagents: 1 gram of 2-thiothymine aldehyde[3]

---

[2] J. H. Kolmer, "Chemotherapy of Bacterial Diseases, The Newer Knowledge of Bacteriology and Immunology," University of Chicago Press, Chicago, Illinois, 1928.

[3] Johnson and Cretcher, J. *Biol. Chem.*, **26,** 99 (1916).

(11), **3** cc. of dimethylaniline and **2** g. of fused zinc chloride. These reagents were mixed and heated in a flask at 100° for four hours. The mixture was stirred intermittently during the heating period. The excess of dimethylaniline was then removed by distillation with steam and the waxy residue left behind washed several times with water and finally dissolved in hot alcohol. On cooling, the leuco compound separated in the form of large, colorless blocks which melted at 212–214° to an oil. The leuco compound is practically insoluble in water. The yield was 1.6 g.

Anal. Calcd. for $C_{22}H_{26}ON_4S$: N, **14.2;** S, **8.1.** Found: **N, 14.1, 14.2;** S, **7.94.**

p-2-Tetramethyldiaminodiphenyl-2-ethylmercaptothyminylmethane, VI.—The procedure followed in preparing this new leuco compound corresponded exactly to that described in the previous experiment for the synthesis of the thio analog. The compound was insoluble in water but very soluble in warm alcohol. It crystallized from the latter solvent in long, colorless needles which melted at 218–219°. The yield was **1.8** g. from one gram of the aldehyde (III).

Anal. Calcd. for $C_{24}H_{30}ON_4S$: N, **13.2.** Found: N, **13.0, 13.1.**

The aldehyde used in this synthesis (III) has already been described in an earlier paper.[3]

p-2-Tetramethyldiaminodiphenylthyminylmethane, IV.—The aldehyde (I) used in the preparation of this compound has likewise been described in our earlier work.[3] The leuco compound was found to be insoluble in water but very soluble in boiling alcohol. It crystallized from the latter solvent in the form of flat prisms or plates and melted at 197–198°. The yield was **1.8** g. from one gram of the pyrimidine aldehyde.

Anal. Calcd. for $C_{22}H_{26}O_2N_4$: N, **14.8.** Found: N, **14.9, 14.8.**

Summary

1. Aldehyde derivatives of thymine condense smoothly with dimethylaniline in the presence of zinc chloride to give stable leuco pyrimidine bases corresponding to the leuco base of malachite green.
2. Their oxidation products will be investigated in this Laboratory.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION]

EFFECT OF HEAT ON MALIC ACID[1]

BY FRED W. MORSE

RECEIVED NOVEMBER 23, 1928 PUBLISHED APRIL 5, 1929

During a study of the cranberry, samples of the fruit were dried before making the subsequent analysis. The berries were cut in halves, spread in thin layers on trays and placed in a large, steam-heated drying-oven, where the temperature ranged around 85°. They remained in the oven for about three days; then they were cooled in the air, weighed, ground in an iron mortar and preserved in bottles.

When total acids were determined in these samples, the results appeared to be low when compared with data obtained from fresh cranberries.

---

[1] Published with the approval of the Director of the Massachusetts Agricultural Experiment Station.

More samples of cranberries were procured. Portions of each sample were weighed, cut in small pieces, placed in volumetric flasks, digested for twenty-four hours with hot water, cooled and made up to volume. Aliquots were withdrawn and titrated. Other portions of the samples were weighed, cut in halves and dried as before. The dried material was pulverized, digested in hot water and aliquots titrated.

The standard alkali used was $N/10$ sodium hydroxide and the indicator was brom thymol blue. Titrations were stopped at the greenish blue tint. The results were calculated as percentages of citric acid in the fresh berries.

Five varieties of cranberries gave an average of 2.26% of total acid in the fresh berries, while the dried portions yielded the equivalent of 1.99% on the fresh basis. Prolonging digestion of the dried material did not change the discrepancy.

The acids of the cranberry have been shown to consist approximately of four-fifths citric acid and one-fifth malic acid[2] while benzoic acid[3] is present as less than 0.1% of the fresh berries.

Nothing has been found in chemical literature to show that citric and malic acids are affected in any manner by heating below 100". Benzoic acid does not account for the loss.

Aberson[4] and Walden[5] have shown that levo-malic acid is partially changed to the anhydride at 100 and 110".

To ascertain the effect of temperatures below 100" upon the principal acids of the cranberry, dilute solutions of citric and malic acids were prepared from selected crystals of each. Several aliquots of each acid were titrated directly. Other aliquots were measured into small beakers. The solutions were evaporated to dryness on the water-bath. Beakers with their films of solidified acids were then placed in ovens where the temperatures were maintained approximately at the following stages: 65°, 75°, 85" and 95°. After various periods of exposure to the respective temperatures, the beakers were removed from the ovens, their contents dissolved in water and the aliquots titrated. The same standard alkali and indicator were used that were described for the cranberries. All titrations were stopped at a light blue tint.

The variations in titrating the citric acid aliquots were within the limits of experimental error, and heating the dried crystals apparently had no effect on the constitution of citric acid.

The aliquots of malic acid yielded such differing results that the crystals appeared to be affected in proportion to both temperature and time of exposure.

---

[2] W. D. Bigelow and P. B. Dunbar, *J. Ind. Eng. Chem.*, 9, 762–767 (1917); also E. K. Nelson, THIS JOURNAL, 49, 1300–1302 (1927).

[3] G. F. Mason, *ibid.*, 27, 613–614 (1905); also N. R. Blatherwick and M. L. Long, *J. Biol. Chem.*, 57, 815–818 (1923).

[4] J. B. Aberson, *Ber.*, 31, 1432–1449 (1898).

[5] P. Walden, *ibid.*, 32, 1706–1721 (1899).

An aliquot of the original solution required 19.1 cc. of the standard alkali. Exposure of the dry acid to 65° for seventy-two hours made no change in the amount of alkali required for an aliquot. At 75° after forty-eight hours an aliquot was neutralized by 18.6 cc. of standard alkali, while another after ninety-six hours required 18.5 cc. At 85° after forty-eight hours an aliquot required 18.5 cc. and after ninety-six hours another was neutralized by 18.0 cc. At 95" 17.8 cc. neutralized an aliquot after twenty-four hours; 12.9 cc. was required after seventy-two hours and at the end of a week an aliquot was neutralized by 10.7 cc.

Walden obtained two anhydrides of I-malic acid. The anhydride obtained at 100° consisted of two molecules of the acid from which one molecule of water had been removed, forming a tribasic acid. The second anhydride was obtained at 180° and consisted of a double molecule with dibasic properties.

The malic acid employed in our experiments was found to be inactive to polarized light and should be regarded as dl-malic acid. A week's heating around 95° of a thin film of the dry acid caused an approach to the second anhydride of Walden, since the alkali required to neutralize the aliquot was but little more than half the amount required for the original solution. Under the conditions of the experiments no definite stages of dehydration were observed.

Walden found that the malic anhydride was restored to the normal acid by heating it with water in a sealed tube at 115°.

Some of the partly dehydrated aliquots were left in the beakers after titration and it was observed that the indicator tint changed to acid. Thereupon watch-glasses were placed on them and the solutions were boiled gently for a few hours with occasional additions of water to maintain the volume of solution approximately constant. The indicator tints were now strongly acid. The solutions were again titrated to the light blue tint. Enough additional standard alkali was required to bring the total for an aliquot up to 18.8 cc. in nearly every one. None could be carried above this figure.

Solutions from the five samples of dried cranberries were next heated after a preliminary titration and titrated a second time. The total alkali required by the two titrations was equivalent to 2.3% of total acid in the fresh berries, thus bringing the dried samples to equality with the undried berries.

Several other samples of dried cranberries were examined in a similar manner but not all of them could be made to yield a total acid equal to the result obtained from the corresponding undried fruit.

Summary

Summing up, malic acid is partly transformed to an anhydride when dried at temperatures between 75 and 95°, the amount of change being dependent on both temperature and time of exposure. Solutions of the partially dehydrated acid, when neutralized by alkali and then boiled for several hours are partially and sometimes completely restored to normal strength. In conclusion, when malic acid occurs in fruits the determination of total acid will be nearest the truth when it is made on undried samples.

Amherst, Massachusetts

[Contribution from the United College of St. Salvator and St. Leonard, University of St. Andrews]

CONDENSATION OF GLUCOSE AND FRUCTOSE. SYNTHESIS OF AN ISO-SUCROSE[1]

By James Colquhoun Irvine, John Walter Hyde Oldham and Andrew Forrester Skinner

Received December 7, 1928 Published April 5, 1929

The investigation of which the results are now communicated has been in progress for some years and was designed to effect the synthesis of sucrose by methods based on researches carried out in this Laboratory on the constitution of mono- and disaccharides.

Prior to the study of methylated sugars initiated by Purdie and Irvine in 1901, no evidence was available regarding the particular form of glucose or of fructose present in sucrose and, in the light of later discoveries, it is not surprising that all attempts to synthesize the disaccharide by the condensation of dextro-rotatory glucose with *levo*-rotatory fructose resulted in failure. In 1903, however, it was shown[2] that when sucrose is methylated and the product hydrolyzed, the form of tetramethylglucose then produced is the same as that obtainable from α-methylglucoside. This result established that one half of the sucrose molecule consists of a glucose residue of normal type but, even at the time, it was evident that the fructose residue was abnormal and differed from the levorotatory form of the sugar. This was obvious from the fact that, on hydrolysis, octamethylsucrose showed no "inversion"[3] and gave a methylated fructose which, contrary to expectation, was dextrorotatory. A further important advance in the chemistry of fructose was subsequently made by Purdie and Paul,[4] who proved that two isomeric tetramethylfructoses exist, one dextro- and the other levorotatory, the reasonable conclusion being that the parent sugar would also display the same isomerism. Some years later Irvine and Robertson[6] brought forward supplementary evidence

---

[1] The results described in this paper were communicated to the Institute of Chemistry (American Chemical Society) in the form of an address delivered on August 3,1928.

[2] Purdie and Irvine, J. *Chem. Soc.,* 83,1036 (1903).

[3] Purdie and Irvine, *ibid.,* 87, 1028 (1905).

[4] Purdie and Paul, *ibid.,* 91, 289 (1907).

[5] Irvine and Robertson, J. *Chem. Soc.,* 109,1305 (1916).

that fructose can exist in a dextrorotatory "y-form" and they expressed the definite opinion that sucrose must be regarded as a derivative of this variety of fructose. The above results were confirmed in the course of other researches conducted in this Laboratory on the constitution of sucrose.[6]

The synthesis of sucrose thus resolves itself into the union, through the loss of water, of equimolecular proportions of normal glucose and y-fructose, or, alternatively, of reducing derivatives of these sugars followed by elimination of the substituting groups. In condensations of this nature the following stereochemical possibilities must be taken into account so that, in all, four isomeric gluco-fructoses may be formed.

1. a-glucose (normal type) may combine with a-fructose (y-type)
2. a-glucose (normal type) may combine-with 0-fructose (γ-type)
3. β-glucose (normal type) may combine with α-fructose (γ-type)
4. β-glucose (normal type) may combine with 0-fructose (γ-type)

No difficulty presents itself in obtaining a convenient derivative of glucose of the desired normal type but it is otherwise in the case of fructose, owing to the uncrystallizable nature and instability of γ-fructose derivatives. However, in the course of examining the acetylation of fructose by the method of Hudson and Brauns,[7] it was shown by Steele[8] that whereas the crystalline fructose tetra-acetate belongs to the stable type, the sirup which yields the crystalline crop consists of a mixture of partially acetylated fructoses containing y-forms. It was hoped that this material although consisting of several compounds might be utilized as a reagent in the synthesis of sucrose [and this has subsequently been done by Pictet[g]] but in view of the importance of the problem we considered it in the highest degree desirable to use individual compounds in preference to mixtures of unknown and variable composition. The experimental obstacles encountered in realizing this program of work have been formidable. It is necessary to describe our experimental procedure in detail as, so far as can be judged, one of the methods traversed by us is precisely the same as that employed by Pictet save that we used a definite tetra-acetylfructose related to y-fructose in place of the mixture of fructose acetates referred to above. Further, the condensations, when successful, yielded an octa-acetate isomeric and not identical with sucrose octa-acetate as the sole crystalline product containing both glucose and fructose residues. We explored, however, more than one method of coupling glucose and fructose, and for these reactions required *(a)* tetra-acetyl-?-fructose and

---

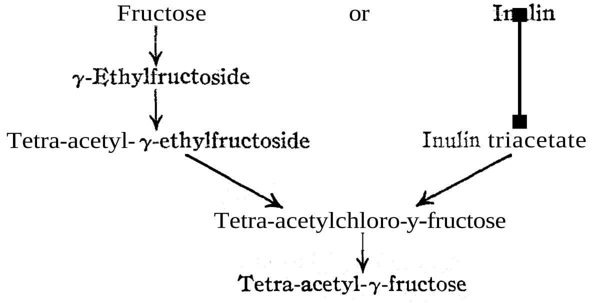
[6] Haworth and Law, *J. Chem. Soc.*, 109, 1314 (1916).

[7] Hudson and Brauns, THIS JOURNAL, 37,2736 (1915).

[8] Steele, J. *Chem. Soc.*, 113, 257 (1918).

[9] Pictet, *Helv. Chim. Acta*, 11, 436 (1928).

(b) tetra-acetylchloro-?-fructose; attention is therefore directed to the experimental part in which the preparation of these new reagents is described according to the following scheme:



At each stage the compounds formed in the above consecutive reactions were converted into tetramethylfructose in order to ascertain if the γ-type remained intact. The results were satisfactory, as the dextro-rotation and properties of the methylated ketose then isolated were in good agreement with the accepted standards for tetramethyl-?-fructose. We have accordingly retained the expression "γ" in the nomenclature of our reagents but wish to emphasize that, as the compounds under consideration are sirups, similarities in rotation and in properties are not sound criteria in establishing identity. The history of methylated sugars shows that fundamental mistakes have been made through hasty claims of this nature and it is undesirable to urge with absolute assurance that our reagents, despite their origin and properties, belong to the same y-fructose type as is present in sucrose.

Three distinct methods of condensation were attempted, *viz.;* A, reaction between tetra-acetylbromo- (or chloro-) glucose and tetra-acetyl-γ-fructose in the presence of a base; B, reaction between tetra-acetylglucose and tetra-acetylchloro-y-fructose in the presence of a base; C, reaction between tetra-acetylglucose and tetra-acetyl-y-fructose in the presence of a dehydrating agent.

It is remarkable that in Method A no condensation of the glucose and fructose residues took place. The halogen derivatives of glucose are conspicuously successful in the synthesis of @-glucosides and their failure to condense with such a reactive compound as tetra-acetyl-y-fructose is significant. On the other hand, the use of tetra-acetylchloro-y-fructose as the halogen-carrying reagent (Method B) was successful and the compound reacted with tetra-acetylglucose to give a crystalline octa-acetyl-*iso*-sucrose (m. p. 131–132°, $[\alpha]_D$ in chloroform + 20.3"). From this, in turn, by de-acetylation an iso-sucrose was isolated in the crystalline state (needles decomposing at 194°, $[\alpha]_D$ in water + 34.2"). The disaccharide, which had no action upon Fehling's solution under standard conditions but gave slight reduction on prolonged boiling, was characterized by greater instability toward acid hydrolysis than sucrose. During hydrolysis a characteristic optical inversion to give "invert sugar" took place.

Precisely similar results were obtained in the case of Method C, the same octa-acetate being formed and, in turn, the same disaccharide. Direct evidence was obtained that other gluco-fructoses were formed in both types of reaction, particularly when tetra-acetylchloro-y-fructose was used as a reagent. In no case, however, did we obtain any crystalline derivative of a gluco-fructose other than that referred to above.

The isomerism of our synthetic disaccharide with sucrose must lie in the stereochemical form (a or β) in which the monosaccharide components are bound together, provided the oxygen ring in the fructose component is actually in the same position as in sucrose. How far this point has been safeguarded has already been discussed. In the case of our tetra-acetyl-y-fructose, which is a sirup, both a- and β-forms are doubtless present and the same holds true for the sirupy form of tetra-acetylglucose used in the condensation, complications which are also present in Pictet's synthesis. As a general rule, however, halogen derivatives of sugars react as β-forms and this fact enables the configuration of iso-sucrose to be deduced with reasonable certainty. As stated, tetra-acetylchloro-γ-fructose yields the acetate of iso-sucrose, a result which presumably stamps the fructose residue as β. On the contrary, tetra-acetylbromoglucose, which is also β, fails to react with the acetate of y-fructose. This might be interpreted as meaning that the a-configuration of glucose is most favorable to condensation with y-fructose but the bulk of the evidence is opposed to this view. The reactions of tetra-acetyl-y-fructose are not exclusively those of a monohydric alcohol and this may be the factor responsible for its failure to condense with halogen compounds. Further, when tetra-acetylchloro-y-fructose is condensed with tetra-acetylglucose, in addition to the compound melting at 131°, a non-crystalline acetylated gluco-fructose is formed which is derived from a disaccharide showing a higher dextro-rotation than sucrose. On the basis of analogy this particular product is a derivative of α-glucoside-β-(γ)-fructose, and the compound melting at 131° must be a derivative of b-glucosido-6-(?)-fructose. Accepting this argument, sucrose must be either α-glucosido-α-(γ)-fructose or β-glucosido-α-(γ)-fructose, preference being given to the latter in view of the magnitude of the rotation of sucrose and the prevalence of β-glucosides in Nature.

Since our preliminary account of the new *iso*-sucrose was published,[10] Pictet[11] has described, under the name "Saccharose D," what may possibly be the same compound.

---

[10] Irvine, *J. Soc. Chem. Ind.*, **47**, 494 (1928).

[11] Pictet, *Helv. Chim. Acta*, **11**, 905 (1928).

	M. p., °C.	$[\alpha]_D$
Iso-sucrose octa-acetate	131–132	+20.3° (in chloroform)
"Saccharose D" octa-acetate	127	+19° (in chloroform)
Iso-sucrose	Sinters at 150° and decomposes without melting at 194°	+34.2° (in water)
"Saccharose D"	127	+19° (in water)

If the compounds are identical, Pictet's preparation must be less pure than that now described and, in any case, his allocation of the β-glucosido-β-(γ)-fructose configuration to "Saccharose D" by application of Hudson's Rule is not convincing. Calculation of the constants required to apply Hudson's Rule demands, for each form of a sugar, a knowledge of the specific rotations of pure crystalline derivatives. Such derivatives, so far as known to us, do not exist in the case of y-fructose.

As stated, we are of the opinion that iso-sucrose is β-glucosido-β-(γ)-fructose but no evidence on this point is afforded by the preparation of the compound by Method C. The condensation of tetra-acetylglucose and tetra-acetyl-y-fructose by shaking in solution with phosphoric anhydride undoubtedly proceeds smoothly and gives a mixture of acetylated disaccharides but has not, in our hands, yielded sucrose octa-acetate as a crystalline component. Consideration will show that each reagent used, in the form in which it is employed, will exist in α- and β-forms, which are capable not only of coupling but of undergoing auto-condensation. In such a reaction there is therefore the possibility that, in addition to the four isomeric glucosido-y-fructoses, there will be formed di-glucoses and di-fructoses, the total number of octa-acetates which may be produced being ten. If the tetra-acetylfructose employed contains the stable stereoisomeride (a factor which is absent in our experiments) this number may be increased to twenty-one. It is, of course, unlikely that all the possible stereoisomerides would react equally in such condensations, but that simultaneous reactions of the above nature can and do proceed is shown by our experience that considerable quantities of iso-trehalose octa-acetate, together with uncrystallizable isomerides, were formed in addition to *iso*-sucrose octa-acetate.

In the course of the research tetra-acetylchloro-y-fructose has been isolated for the first time and as this compound is obviously a valuable reagent in the study and synthesis of fructose derivatives, we desire to reserve its application and also those of the tetra-acetyl-y-fructose described by us.

Experimental

For the purposes of this investigation the following compounds were required: (1) tetra-acetyl-y-fructose, (2) tetra-acetylchloro-y-fructose and **(3)** tetra-acetylglucose.

Preparation of **Tetra-acetyl-γ-fructose** from Fructose. Stage I. **γ-Ethylfructoside.**—The following is an account of **a** typical preparation. Sixty-five grams of finely-powdered fructose was dissolved in 2285 cc. of hot absolute alcohol and, after cooling, 250 cc. of alcohol containing 26 g. of anhydrous hydrogen chloride was added. The progress of the condensation was followed polarimetrically, the rotation rapidly altering to dextro and attaining in about ten minutes the maximum value $[\alpha]_{\mathrm{D}} = +17^\circ$ (approx.). The reaction was arrested as closely as possible to this maximum value, absolute alcohol, in which 18 g. of sodium had been previously dissolved, then being added. Carbon dioxide was passed through the alkaline liquor, which was thereafter evaporated under diminished pressure and the sirupy residue dried at 100° (12 mm.). This was extracted repeatedly under a reflux condenser with a mixture of ethyl acetate and alcohol until the undissolved material disintegrated into a hard red powder. The solution was then taken to dryness and the residue extracted repeatedly with dry ethyl acetate at the boiling point. On standing overnight in a corked flask a sirup was deposited from the solution and on decantation and removal of the solvent, γ-ethylfructoside remained as a sirup. It is important to note that the subsequent acetylation of the ethylfructoside should be undertaken promptly, as if the material is allowed to stand for more than twenty-four hours the acetate subsequently obtained is a hard glass and is apparently a polymeride.

Stage **II.** Acetylation of **γ-Ethylfructoside.**—This reaction was carried out in the usual manner with acetic anhydride and sodium acetate, the acetylated mixture being poured into water and nearly neutralized with calcium carbonate. Thereafter the liquid was shaken with excess of benzene, which was separated and washed with 1% sodium hydroxide until the alkaline extracts were nearly colorless. After washing with water, drying over sodium sulfate and decolorization with Norite, the benzene was removed and the residue dried at 100° (12 mm.). In this way tetra-acetyl-y-ethylfructoside was obtained as a colorless, mobile sirup, the yield from 65 g. of fructose ranging from *33* to 47 g. As the preparation yielded a mixture of ***a***- and β-forms, the specific rotation varied slightly in different preparations, the extremes being $[\alpha]_{\mathrm{D}}$ $+39.0^\circ$ and $+47.9^\circ$ in chloroform solution $(c = 5)$; n_{D} varied from 1.4528 to 1.4542.

Anal. Calcd. for $C_{16}H_{24}O_{10}$: C, 51.06; H, 6.38; OC_2H_5, 11.9; CH_3CO, 45.7. Found: C, 51.09, 50.75, 50.84; H, 6.36, 6.51, 6.42; OC_2H_5, 11.1, 11.8; CH_3CO, 46.3, 47.5.

For the purpose of confirming that the compound was actually a derivative of fructose, it was converted under quantitative conditions into the parent monosaccharide, a weighed quantity of the acetate being dissolved in methyl alcohol and boiled for fifteen minutes with more than the calculated amount of normal sodium hydroxide. Thereafter the alkali was neutralized and sufficient hydrochloric acid added to make the total acid concentration $N/10$. The solution was then boiled under a condenser in the presence of a small quantity of Norite and after thirty-five minutes the value $[\alpha]_{\mathrm{D}}$ -84.1° was recorded, the concentration being calculated on the basis of complete conversion into fructose. In a control experiment in which pure fructose was boiled with the same concentration of aqueous acid the value $[\alpha]_{\mathrm{D}}$ −85.8" was obtained in the same time. Similarly, a sample of tetra-acetyl-y-ethylfructoside when subjected to consecutive alkaline and acid hydrolysis gave 99% of the weight of glucose phenylosazone obtained in a control experiment carried out with the equivalent amount of pure fructose.

Stage **III. Hydroxylation** of **Tetra-acetyl-γ-ethylfructoside.**—A 10% solution of tetra-acetyl-y-ethylfructoside in acetyl chloride was saturated with dry hydrogen chloride and allowed to stand at room temperature for eighteen hours. When the reaction was complete, as indicated by the attainment of a constant rotation, the solvent was removed under diminished pressure at a temperature not exceeding 45°. The residue was dried, weighed, dissolved in benzene and an amount of silver oxide equal in weight to that of the sirup added together with a small quantity of water. The mixture was then shaken until a sample of the liquid gave no precipitate when diluted with alcohol and boiled with an alcoholic solution of silver nitrate. Water was removed by means of sodium sulfate, the solids were filtered and washed with benzene, the total filtrate being shaken with water until the extracts gave only a slight reduction with Fehling's solution. Thereafter the united aqueous extracts were shaken repeatedly with chloroform, which was separated and dried over sodium sulfate. Care had to be taken to carry out this extraction with chloroform promptly as otherwise the yields were seriously impaired. On removal of the solvent an almost colorless sirup remained which was dried at 100° (12 mm.) and consisted of tetra-acetylfructose.

Anal. Calcd. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.74; CH_3CO, 49.4. Found: C, 48.18, 48.10; H, 5.90, 5.79; CH_3CO, 50.8; $[\alpha]_D$ in chloroform, $+31.5°$ for $c = 1.808$, and in benzene, $+38.7°$ for $c = 5.379$; $n_D = 1.4645$.

Preparation of Tetra-acetyl-y-fructose from Inulin.—Inulin is a convenient source of tetra-acetyl-y-fructose but the product is not so pure as when made from ethylfructoside and the process cannot be so accurately described in view of the variations shown by specimens of triacetylinulin prepared by different methods. A 10% solution of triacetylinulin in acetyl chloride was saturated with hydrogen chloride, polarimetric readings of the solution being taken at intervals. Using triacetate prepared by Pringsheim's method the specific rotation increased in four days to a value between +60° and +70°. The further procedure was exactly as described in Stage III of the preceding preparation although it proved necessary to repeat the successive treatment with benzene and with chloroform in order to obtain a colorless product. In a typical experiment 42 g. of inulin triacetate gave 32.8 g. of tetra-acetyl-y-fructose together with 3.4 g. of a crystalline triacetyl anhydro-fructose.[12]

Anal. Calcd. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.74; CH_3CO, 49.4. Found: C, 47.87, 47.94; H, 6.05, 5.95; CH_3CO, 49.6; $[\alpha]_D$ in chloroform, $+37.8°$ for $c = 1.838$; $n_D = 1.4662$.

Tetra-acetyl-y-fructose shows a wide range of solubility in organic solvents and differs from the form described by Pictet in rotation and in being soluble in dry ether.

Tetra-acetyl-y-fructose.—It is evident that by both the methods described above a form of tetra-acetylfructose is obtained isomeric with the crystalline tetra-acetylfructose of the stable type. In order to show that both preparations were derivatives of fructose, weighed amounts of each were dissolved in water containing ice and a measured excess of 2 N sodium hydroxide was added. The acetyl groups were completely removed when the solution was allowed to stand immersed in ice water for twenty minutes

---

[12] This crystalline derivative of fructose, hitherto undescribed, was first encountered in the course of a separate research conducted in this Laboratory, the results of which will shortly be published. The compound remains behind when the benzene extract of tetra-acetylfructose is evaporated to dryness and can be obtained crystalline from the alcohol extract of the sirup.

and the excess of alkali was then estimated. Thereafter the solution was diluted to a known volume and the rotation determined. In a control experiment crystalline tetra-acetylfructose of the stable type was similarly treated, the results being:

		Acetyl content	$[\alpha]_D$
Crystalline tetra-acetylfructose		51.1	−92.4"
Tetra-acetyl-γ-fructose	From ethylfructoside	50.8	−89.8
	From inulin	49.6 (calcd. 49.4)	−89.4

As, moreover, the three compounds specified above gave yields of glucose phenylosazone comparable with that given by the equivalent weight of fructose, there can be no doubt that they are derived from this monosaccharide.

Evidence that the Dextrorotatory Tetra-acetylfructose is Derived from γ-Fructose.—Tetra-acetylfructose prepared from inulin was methylated by the action of methyl iodide and silver oxide until the reaction on Fehling's solution disappeared. The tetra-acetylmethylfructoside thus produced was then de-acetylated by the action of sodium methylate and the alkylation completed in the usual manner. In this way tetramethylmethylfructoside was formed in nearly quantitative amount and on hydrolysis by means of *N*/100 hydrochloric acid was converted into tetramethylfructose. Analysis of a distilled sample gave: C, 50.72; H, 8.59; OCH_3, 51.2. Calcd. for $C_{10}H_{20}O_6$: C, 50.84; H, 8.47; OCH_3, 52.5.

Comparison of the product with a sample of tetramethyl-γ-fructose obtained from methylated sucrose showed that the compounds displayed so close a similarity that they may be regarded as identical. The refractive indices (n_D = 1.4533) were the same and the specific rotations in water for $c = 5$ although not identical were dextro and of the same order.

	Tetramethylfructose from tetra-acetylfructose	Tetramethylfructose from octamethylsucrose
Initial $[\alpha]_D$	+26.4°	+31.8°
After 3 days	+30.1	+34.1
After 5 days	+30.1	+34.1

Taking into consideration the possibility that coincidence or similarity of optical rotations determined on liquid compounds may be fortuitous, the comparison of the two specimens of tetramethylfructose was further extended. Sodium derivatives of each were prepared by the method of Freudenberg[13] and the products showed the characteristic optical inversion, in each case the value of $[\alpha]_D$ being of the order −45°. In addition, the behavior of the two sugars when condensed with methyl alcohol was compared and likewise the rate of hydrolysis of the two specimens of tetramethylmethylfructoside thus produced. Two series of experiments were made. In one of them, 5% solutions of the two tetramethylfructoses in

---

[13] Freudenberg, Ber., 56, 1119 (1923).

methyl alcohol containing 0.1% of hydrogen chloride were preserved at 15° and polarimetric records taken, initially at intervals of a few minutes and afterwards at hourly periods. The curves obtained on plotting the optical values against time were parallel (Fig. 1), although the specimen of methylated fructose prepared from sucrose showed throughout a higher dextro specific rotation of four degrees. A similar result was obtained in a second experiment in which the acid concentration was increased to 0.25% and the characteristic fall and rise of dextrorotation in the early stages of the reaction was observed in each case. In addition, the polarimetric curves representing the condensation were strictly parallel, as shown in Fig. 2.

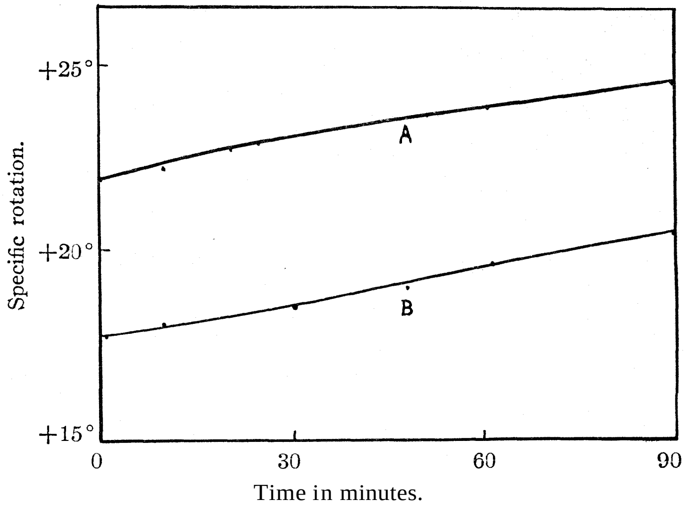


Fig. 1.—Condensation of tetraniethylfructose with methyl alcohol. Acid concentration = 0.1%. T = 15°. A. Sugar obtained from sucrose. B. Sugar obtained from tetra-acetylfructose.

The specimens of tetramethylmethylfructoside produced in the reaction were isolated in the usual manner and distilled in a high vacuum, the refractive index and methoxyl content showing that the compounds were pure. Thereafter in parallel experiments the methylated fructosides were hydrolyzed by the action of *N*/100 hydrochloric acid at 85°. The polarimetric records of the hydrolysis were identical, as shown in Fig. **3,** thus affording substantial evidence that the tetra-acetylfructose now under consideration is a y-form.

Preparation of Tetra-acetylchloro-y-fructose.—Although tetra-acetylchloro-y-fructose may be obtained by the action of acetyl chloride on tetra-acetyl-y-ethylfructoside, tetra-acetyl-7-fructose is a more convenient starting-material. A 9% solution of this compound in acetyl chloride was saturated with dry hydrogen chloride and polarimetric observations were taken at short intervals. The specific rotation, which was initially +47.7°, increased rapidly, the maximum value of +56.5° being attained in about thirty minutes. At this stage the solvent was removed under diminished pressure at a temperature which must not exceed 45° and a mobile sirup remained which was dissolved in benzene. The solution was allowed to stand over potassium carbonate and on removal of the solvent a sirup remained which was essentially tetra-acetylchloro-?-fructose. Owing to the instability of the compound no further purification was possible. On the basis of analysis the mixture contained 87% of the chloro derivative and this was confirmed by conversion of the compound by standard methods into tetra-acetyl-y-fructose and tetra-acetyl-γ-ethylfructoside, respectively.

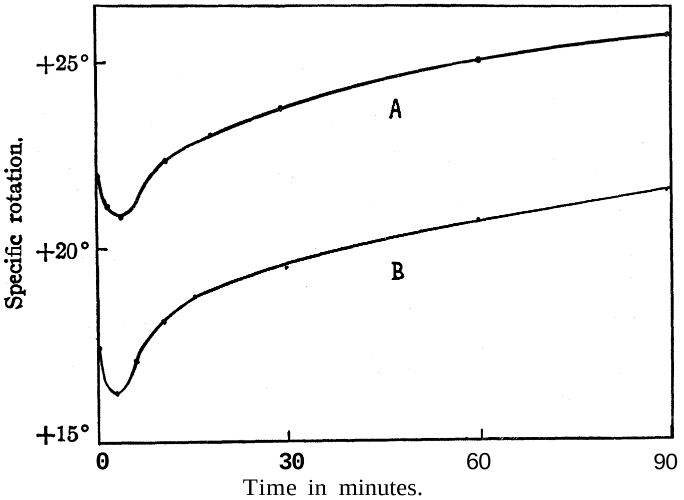


Fig. 2.—Condensation of tetramethylfructose with methyl alcohol. Acidconcentration = **0.25%.** T = 15°. A. Sugar obtained from sucrose. B. Sugar **obtained** from tetra-acetylfructose.

Preparation of **Tetra-acetylglucose.**—The method described by Fischer[14] was slightly modified. Tetra-acetylbromoglucose was dissolved in acetone and as much water added as was possible without causing precipitation. The solution was then shaken under thorough cooling with excess of silver oxide until a test portion showed that all bromine had been eliminated. The bulk of the acetone was removed under diminished pressure, excess of cold water was added and the solution extracted twice with benzene which in turn was extracted with water. The united aqueous solution and washings was shaken with chloroform, a good yield of glucose tetra-acetate being isolated from the extract in the usual way. The prod-

---

[14] Fischer, Ber., 42,2778 (1909).

uct crystallized on mixing with dry ether, the soluble sirupy variety which was used in the condensation experiments thereby passing into solution.

Condensation of Tetra-acetyl-γ-fructose with Tetra-acetylglucose.—This reaction was carried out under varying conditions, the union of the glucose and fructose residues being conducted in benzene solution by the agency of phosphoric anhydride. As the crystalline variety of tetra-acetylglucose is very sparingly soluble in benzene the non-crystalline tetra-acetyl glucose was employed. Equal weights of the glucose and fructose acetates were dissolved in benzene to give a total concentration of solids not exceeding 10%. Excess of phosphoric anhydride was added and the liquid thoroughly shaken, care being taken to ensure that the phosphoric anhydride did not settle to the bottom of the vessel. In no case did the reducing action upon Fehling's solution entirely disappear and the optimum time at which to arrest the reaction could be ascertained only by experience, but as a rule it was necessary to continue shaking for at least fifteen hours. The benzene solution was decanted and exhaustively extracted with water until the washings no longer reduced Fehling's solution. This treatment removed unchanged glucose and fructose tetraacetates, which were recovered by extracting the water with chloroform.

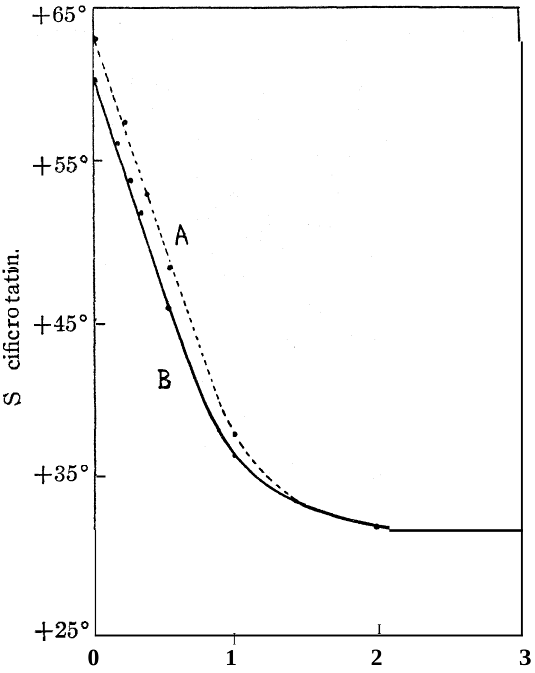


Fig. %.—Hydrolysis of tetramethylmethylfructoside. Acid concentration = 0.36%. T = 85°. A. From sucrose. B. From tetra-acetylfructose.

The benzene was again washed, first with 1% sodium hydroxide and then with water, dried over sodium sulfate and taken to dryness under diminished pressure at a temperature not exceeding 60°. On stirring the residue with dry ether, crystals separated which were filtered, washed with ether and recrystallized from absolute alcohol. The compound, which proved to be an octa-acetyl-iso-sucrose, melted at 131–132°. Although this octa-acetyl-iso-sucrose was the only crystalline gluco-fructose derivative which was isolated, it was ascertained that iso-trehalose was formed simultaneously. Moreover, the yields of disaccharide derivatives were invariably small, the bulk of the materials originally employed remaining uncondensed. This is shown by the following table.

Tetra-acetylfructose and -glucose, g.........	46	34.9	22.0	16.0	85.0	56.0
Acetylated monosacch. recov. unchanged, g....	34.9	22.0	16.0	4.9	56.0	..
Acetylated disaccharides, g................	7.7	4.3	4.0	7.2	10.0	9.0
Octa-acetyl-iso-sucrose (m. p. 131–132°), g....	(.......1.7......)			2.0	1.0	1.5

The investigation of the acetylated disaccharides other than *iso*-sucrose octa-acetate is being continued.

Condensation of Tetra-acetylchloro-γ-fructose with **Tetra-acetylglucose.**—To a solution of 27 g. of the chloro compound and 30 g. of sirupy tetra-acetylglucose in 135 cc. of dry chloroform were added sodium sulfate and excess of silver carbonate. The liquid was shaken until no chlorine remained in solution and after filtration the solvent was removed. On dissolving the residue in benzene and extracting repeatedly with water, reducing sugars were eliminated for the most part, while the condensation products, together with penta-acetylglucose, remained dissolved in the benzene. The solvent was evaporated, the residue dissolved in alcoholic dimethylamine and heated at 100° for three hours, reducing sugars being destroyed by the action of the base while disaccharides remained unaffected. On removal of the solvent the discolored sirup was extracted successively with ether, acetone and chloroform, most of the coloring matter thereby passing into solution. The residue was then acetylated to convert any non-reducing disaccharide into octa-acetate.

Examination of the Mixture of Disaccharide Octa-acetates.—A sample of the sirupy product, 'before the separation of the octa-acetate of *iso*-sucrose referred to below, was hydrolyzed under standard conditions by the successive action of alkali and acid. After removal of the acetyl groups the specific rotation was $+65.9°$, a value which is practically identical with that of sucrose. Moreover, on heating subsequently at 100° with *N*/10 hydrochloric acid the end-point $[\alpha]_D$ -16.4" was obtained while a control experiment carried out on sucrose gave under identical conditions $[\alpha]_D$ $-19.1°$. This result proves that the disaccharide acetates under examination were convertible into "invert sugar" but the mixture, on crystallization from ether, yielded one-third of. its weight of the crystalline *iso*-sucrose octa-acetate (m. p. 131–132°) already described. As the *iso*-sucrose corresponding with this acetate shows, when liberated under the same conditions, $[\alpha]_D$ $+31.2°$, it follows that the identity of the activity of the total product with that of sucrose must be fortuitous. Further, even if sucrose be formed in the condensation under discussion, a third isomeric gluco-fructose showing a specific rotation substantially higher than $+65.9°$ must also be present.

Octa-acetyl-iso-sucrose.—This compound prepared by either of the methods described above is the only crystalline derivative of a non-reducing gluco-fructose isolated by us. It dissolves readily in hot ethyl or methyl alcohols, chloroform or acetone, is sparingly soluble in benzene or ether and is insoluble in water. When recrystallized from hot alcohol it separates in prisms.

Anal. Calcd. for $C_{28}H_{38}O_{19}$: C, 49.55; H, 5.60; CH_3CO, 50.7; mol. wt., 678. Found: C, 49.41; H, 5.61; CH_3CO, 53.0; mol. wt. in chloroform by boiling-point method, 687.

The fact that the sugar suffers slight decomposition in the presence of alkali accounts for the high acetyl value.

Solvent	Chloroform	Acetone	Benzene
c	3.762	4.072	3.918
$[\alpha]_D$	+19.9°	+20.0°	−2.0°

Iso-sucrose.—A 20% solution of crystalline octa-acetyl-iso-sucrose in absolute ethyl alcohol containing 30% of dimethylamine was heated for 150 minutes at 100° in a sealed tube. After removal of the solvent, the residue was dried at 100° (12 mm.). On dissolving this residue in the minimum amount of methyl alcohol and adding a small quantity of ethyl alcohol, a dense crop of crystals separated. These were recrystallized from the same medium, normally in the form of needles, occasionally as prisms which sintered at 152°, and decomposed sharply at 194° (uncorrected). When the sirup present in the united mother liquors was isolated, dissolved in ethyl alcohol and precipitated with ether, the total yield of de-acetylated sugar was almost quantitative.

Anal. Calcd. for $C_{12}H_{22}O_{11}$: C, 42.10; H, 6.43. Found: C, 42.09; H, 6.51.

In solubility and in crystalline form this variety of iso-sucrose displays a very close similarity to sucrose the difference between the two disaccharides being shown by the melting point and by the fact that this particular isomeride of sucrose is slowly decomposed on prolonged boiling with alkali and gives a small yield of glucose phenylosazone under standard conditions. The specific rotation is also markedly different from that of sucrose.

Solvent	*c*	$[\alpha]_D$
Methyl alcohol	2.130	+50.0° without mutarotation
Water	5.264	+34.2° without mutarotation

Inversion of the Iso-sucrose.—Although the form of iso-sucrose was devoid of action upon Fehling's solution for a normal period of boiling, prolonged heating occasioned a slight reduction. This indicates a greater instability toward hydrolysis than in the case of sucrose, a view which was supported by the behavior of the compound on acid hydrolysis. When heated at 100° with $N/1000$ hydrochloric acid, inversion took place, the specific rotation rapidly altering to levo and attaining the constant value

—19.2'. Under parallel conditions sucrose was hydrolyzed much more slowly, as shown from the figures quoted below:

Time, min.	Iso-sucrose	Sucrose
Initial	+32.8°	+66.3°
30	−16.0	+ 4.4
60	−18.2'	− 7.2
90	−19.2" (constant)	.....
100	− 19.8	−13.4
135	− 19.6	-15.5^a
165	.....	-17.2^a
195	.....	−19.2

c =2.038; acid, N/1000 HCl; T = 100".

[a] $[\alpha]_D$ recalculated for change of concentration.

The end-point is thus the same as that given by sucrose and the hydrolysis solution behaved exactly as a solution of "invert sugar" in that the optical activity vanished on heating to 80°. The yield of glucose phenylosazone from the hydrolysis liquid was also the same as that obtainable from invert sugar in equal concentration.

The thanks of the authors are due to the Carnegie Trust for Research Fellowships which enabled two of the collaborators to take part ~~in the~~ investigation.

Summary

1. For the purposes of the research, pure tetra-acetyl-y-fructose and tetra-acetylchloro-y-fructose have been prepared for the first time, and their relationship to y-fructose established by the methylation method.

2. In attempts to synthesize sucrose from these reagents the following reactions have been carried out: *(a)* condensation of tetra-acetylchloro-γ-fructose with tetra-acetylglucose in the presence of a base, (b) condensation of tetra-acetyl-y-fructose with tetraacetylglucose in the presence of a dehydrating agent.

3. In each case the only crystalline product isolated was an *iso*-sucrose octa-acetate (m. p. 131–132'; $[\alpha]_D$ +20.3° in chloroform). No sucrose octa-acetate was detected, although evidence was obtained that acetylated gluco-fructoses other than *iso*-sucrose octa-acetate and also diglucoses were formed.

4. The mixed products obtained in the above condensations gave a specific rotation practically identical with that of sucrose and are convertible quantitatively into "invert sugar." This result is, however, fortuitous.

5. Iso-sucrose has been isolated as needles decomposing at 194° and showing $[\alpha]_D$ $34.2' in water. The compound is hydrolyzed more readily than sucrose and is then converted into "invert sugar."

6. No union of glucose and fructose residues takes place when tetra-acetylbromoglucose is shaken in solution with tetra-acetyl-y-fructose.

7. The collective results lead to the conclusion that sucrose is β-glucosido-α-(γ)-fructose and that the iso-sucrose now described is β-glucosido-β-(γ)-fructose.

ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. II.
REDUCTION OF ISOPRENE BY $Na-NH_3$

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The reduction of isoprene by sodium in liquid ammonia was attempted to determine: (1) whether reduction would take place in preference to polymerization and **(2)** the location of the added hydrogen.

Isoprene was added to sodium dissolved in liquid ammonia and a 60% yield of 2-methyl-2-butene resulted. No other volatile hydrocarbon was found. High molecular weight hydrocarbons were formed but were not investigated. It is thus shown: (1) that the predominant reaction proceeds in accordance with the equation $C_5H_8 + 2Na + 2NH_3 = C_5H_{10} + 2NaNH_2$ and (2) that hydrogen adds to isoprene in the 1,4-position, in agreement with Thiele's theory.

The hydrogen addition is similar to the bromination of isoprene at low temperature.[1] If properly conducted the latter reaction stops after 2 atoms of bromine have been added to 1 molecule of isoprene; the resulting compound, 1,4-dibromo-2-methyl-2-butene, is characterized by the inactivity of its double bond toward bromine. Similarly, 2-methyl-2-butene obtained by reduction of isoprene is not reduced to isopentane by an excess of $Na-NH_3$ reagent.

Procedure.—750 cc. of liquid ammonia are placed in a one-liter round-bottomed flask (Pyrex) and 46 g. of sodium is dissolved in it. The flask is equipped with a rubber stopper carrying a separatory funnel and an abduction tube. One mole of isoprene is slowly dripped into the liquid; the stem of the separatory funnel should nearly reach the surface of the ammonia in order to prevent abduction of isoprene by the escaping ammonia vapors. When the isoprene drops strike the ammonia, a clear sound is heard which can be used to regulate the delivery. The ammonia vapors carry the reduced hydrocarbon, together with a small quantity of unchanged isoprene, through an empty safety bottle to a cylinder filled with cracked ice. Ammonia dissolves immediately, the ice melts and the water flows into a large separatory funnel; the hydrocarbon, which condenses on the ice, is carried with the water and collects as an upper

---

[1] Staudinger, *Helv. Chim. Acta*, 5, 756–767 (1922).

layer in the separatory funnel. By rerunning, the hydrocarbon can be completely freed of isoprene.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. III. DIMETHYLOCTADIENE

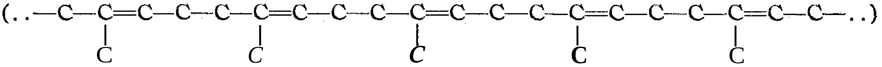
BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The polymerization of isoprene to synthetic rubber has long been known. The mechanism of this reaction has, however, so far escaped detection. To throw light upon this question, it was decided to polymerize isoprene in the presence of active hydrogen, with the hope that polymerization might be stopped at the dimer stage. This was accomplished in the following manner.

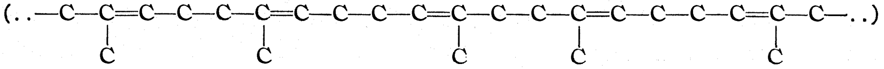
Well-purified isoprene, active toward polymerization, was placed in contact with metallic potassium chips and ethyl alcohol slowly added at a rate just sufficient to give a moderate evolution of hydrogen at the surface of the potassium. A good yield of a light yellow oil resulted, which upon analysis proved to be a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,G-octadienes. These isomers are the dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- or the 1,1-carbon atoms, respectively, and the addition of hydrogen to the 1,8-positions of the dimer. No trace of a compound of cyclic nature could be detected.

These results suggest that the polymer of isoprene produced by contact with alkali metals and called "sodium rubber" (the commonest of the synthetic rubbers) is a long chain formed of isoprene units linked together by means of their 1 and 4 carbon atoms. This chain very closely resembles the long-chain structural formula of natural rubber proposed by Staudiiger[1] and his associates, except that the recurring methyl groups may be placed at either side of the double bond, thus



$$(..\text{—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—}..)$$

Section of the natural rubber molecule (Staudinger)



$$(..\text{—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—C=}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{—C—C—}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{=C—C—C—C=}\underset{\overset{|}{\mathrm{C}}}{\mathrm{C}}\text{—C—}..)$$

Section of the synthetic rubber molecule

It should be noted that in the natural product the groups attached to each double bond may be expected to present always the same *cis-* or trans-configuration, whilst such uniformity can hardly be hoped for in the synthetic product.

---

[1] **Staudinger, *Helv. Chim. Acta*, 5, 785–805 (1922), and later papers.**

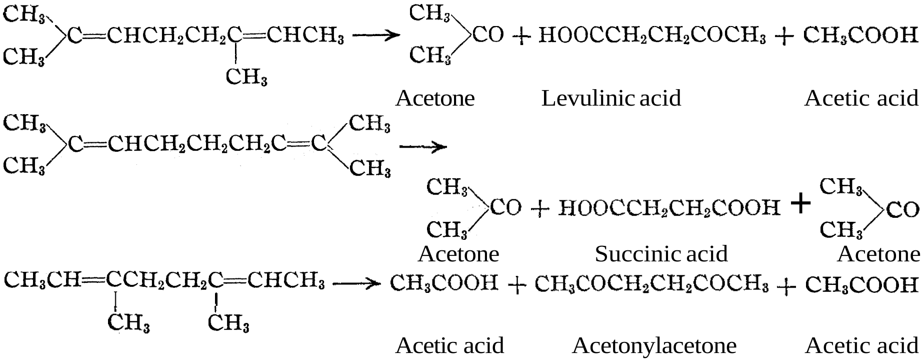
The products of the side reactions appear to be high polymers; their constitution is being studied at the present time. It is thought that a small amount of 2-methyl-2-butene was formed during the reaction but it was lost with the escaping hydrogen excess.

Procedure.—The apparatus comprises a 500-cc. round-bottomed flask equipped with a reflux condenser and a separatory funnel. The top of the condenser is connected to a glass tube whose end dips into a test-tube containing a little alcohol, thus making it possible to judge the rate at which hydrogen escapes.

Two-gram molecules of isoprene were placed in the flask, 4-g. atoms of potassium shavings quickly added and the flask connected to the condenser and separatory funnel; alcohol was dripped in at such a rate that a hydrogen excess escaped slowly from the apparatus. During the reaction the potassiuin remained shiny; when it was completely used, the potassium ethylate formed during the reaction was decomposed by adding water slowly through the separatory funnel. The reaction product was decanted, washed, dried and distilled. The mixture of dimethyloctadienes had the following constants: b. p., 163–167°; d_{20}^{20}, 0.769; n_D^{20}, 1.4457; mol. wt., 136.8 (138, theoretical). The bromination number determined with a $KBrO_3$–KBr mixture gives 2 double bonds per $C_{10}H_{18}$. Combustion checks the previous formula. Hydrogenation requires 2 moles of hydrogen and yields 2,6-, 2,7- and 3,6-dimethyloctanes.

Analysis of the **Dimethyloctadienes.**—The hydrocarbon was oxidized by means of a solution of CrO_3 in acetic acid. After removal of the bulk of Cr_2O_3 as $Cr_2(SO_4)_3$, insoluble in H_2SO_4, the following products were detected: acetone, 2,5-hexanedione, levulinic acid and succinic acid. These compounds are all very easily characterized: acetone by means of its mercury compounds, acetonylacetone by its dioxime and its unusually strong reaction with bromine, levulinic acid by its reaction with sodium nitroprusside and succinic acid by the pyrrole–pine shaving reaction.

The following diagram compares the oxidation products with the hydrocarbons from which they are formed.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CHCH_2CH_2\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO + HOOCCH_2CH_2COCH_3 + CH_3COOH$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CHCH_2CH_2CH_2C{=}C\!\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO + HOOCCH_2CH_2COOH + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO$$

$$CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_2\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 \longrightarrow CH_3COOH + CH_3COCH_2CH_2COCH_3 + CH_3COOH$$

Although one of the oxidation products probably was acetic acid, it is obvious that it could not be detected, since the oxidation was carried out in an acetic acid solution. It is nevertheless evident that the hydrocarbon obtained by polymerization and simultaneous reduction of isoprene is a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes.

Summary

The dimer of isoprene formed under conditions which normally produce "sodium rubber" has been stabilized by the addition of hydrogen. This partially hydrogenated dimer is a mixture of three isomeric dimethyloctadienes; its formation indicates that the mechanism of the polymerization of isoprene to synthetic rubber is the joining of many isoprene molecules by linkage of the 1,1-, the 1,4- or the 4,4-carbon atoms to produce a long-chain molecule.

ITHACA, NEW YORK

NEW BOOKS

Annual Survey of American Chemistry. Vol. III, July 1,1927, to July 1, 1928. Edited by CLARENCE J. WEST. Prepared under the auspices of the Division of Chemistry and Chemical Technology, National Research Council. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 395 pp. 13.5 × 21.5 cm. Price $3.00.

This volume of the Survey contains forty-six chapters which deal with the more actively studied fields in chemistry. A change in policy by the editorial board is announced in the foreword. This consists in "varying the subjects treated from year to year, which will mean that certain less active fields will be covered only every second or third year. Different authors also will be asked to write the reviews, thus distributing the effort of preparing the chapters among the authorities in the fields involved, and giving the readers more than one man's point of view on a particular subject."

The last volume of the Survey is well up to the standard of the former ones. The book is invaluable to one who wishes to keep in touch with the remarkable advance in research in chemistry in this country.

JAMES F. NORRIS

Gmelins Handbuch der anorganischen **Chemie.** (**Gmelin's** Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition, completely rewritten. Sodium. System No. 21. Issued by the Deutsche Chemische Gesellschaft. Verlag **Chemie,** G. m. b. H., Corneliusstrasse 3, Berlin, W 10, Germany; 1928. 18 + 33 + 992 pp. 75 figs. 17 × 25 cm. Price, to subscribers, M. 118; singly, M. 150 (postage included).

This is the largest volume so far published in this encyclopedia of inorganic chemistry. It contains almost a thousand pages, exclusive of the extensive table of contents. In accordance with the scheme of treatment followed throughout the encyclopedia, it first discusses sodium itself and then all of the compounds of sodium with elements bearing a lower number in the arbitrary numerical series that has been adopted.

The text is replete with many hundreds of tables of numerical data and with many skilfully executed diagrams. One cannot but be impressed first with the tremendous amount of human effort that has been devoted to the investigation of even this limited corner of the universe, and second with the industry, patience and understanding which the succinct recapitulation of all this information has required.

Particular features are the forty page account of the occurrence of sodium compounds; the eighty-five page account of the physico-chemical properties of the element and the sixty page account of sodium chloride. The literature has been covered up to January 1, 1928.

We cannot but he grateful to the editor and to the numerous staff of collaborators who have been responsible for this excellent and valuable volume.

ARTHUR B. LAMB

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition, revised. Radium and its Isotopes. System No. 31. By OTTO ERBACHER. Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany; 1928. xxii + 80 pp. 4 figs. 17 X 25 cm. Price, to subscribers, M. 12; singly, M. 15.

This volume is the smallest of the series so far. At first blush this small size appears surprising when one recalls the immense amount of study which has been devoted to radium. On further thought, one realizes that partly because of the short time that has elapsed since its discovery and more because of its great rarity, little actual study of the chemical behavior of radium or of the properties of its compounds has been made. Moreover, its radioactive properties are of such transcendently greater interest that the investigation of the ordinary chemistry of radium has doubtless seemed hardly worth while. Indeed, an inspection of this book shows that only about a score of radium compounds have so far been made.

The literature has been covered up to January 1, 1928.

ARTHUR B. LAMB

Symbols and Formulae in Chemistry. By R. M. CAVEN, D.Sc., F.I.C., Professor of Inorganic Chemistry in the Royal Technical College, Glasgow, and J. A. CRANSTON, D.Sc., A.I.C., Lecturer in Physical Chemistry in the Royal Technical College, Glasgow. Blackie and Son, Ltd., London and Glasgow, England, 1928. ix + 220 pp. 15 X 22.5 cm. Price, 15s., net.

According to the title page this book is an historical study of symbols and formulas in chemistry. In reality the growth of the ideas represented by the symbols and formulas is illuminatingly traced; this is, of course, as it should be, and the book is really a history of the growth of chemical ideas.

For example, the rise and fall of the dualistic theory of Berzelius is sympathetically and fully discussed, even though there were but few symbols specifically applied to this theory. The tenacious adherence of Berzelius to what he was convinced was the truth, and what really embodied the truth in a vague sort of way, is vividly set forth; also his inability to support his theory against the unitary view of Dumas just because he could not grasp a clear conception of a relation between matter and electricity. It needed but the recognition of the adding or subtracting of discrete charges of electricity later to bring the dualistic theory into its own again; in fact, the modern study of the electron in chemistry is but the culmination of Berzelius' ideas of dualism.

The various modern ideas concerning the function of the electron in chemical structure and valence are briefly but adequately and impartially presented and the great confusion arising from the contradictory meanings with which modern theorists use old symbols in fashioning their formulas is noted. The idea suggests itself to the reader that perhaps the modern theories are suffering, just as did Berzelius' theory, from a failure to grasp some elusive but probably very simple and clarifying conception.

ARTHUR A. BLANCHARD

Problbmes et calculs de chimie générale, recueil destine aux élèves des grandes écoles et aux étudiants en chimie. (Problems and Calculations of General Chemistry, a Compilation for Students in Advanced Schools and Students of Chemistry.) By R. HOCART, Licencié in the Physical Sciences. Preface by H. Copaux. Gauthier-Villars et Cie., 55 Quai des Grands-Augustins, Paris, France, 1928. x + 181 pp. 14 figs. 14 × 22.5 cm. Price, 30 fr.

The problems here set forth were first presented in a series of lectures by M. Hocart. Each chapter begins with a brief presentation of the fundamental principles and follows with a large number of carefully selected problems. As a collection of problems the volume is unique in that a complete solution is given for every problem presented, together with a reference to the literature in many cases. The large variety in the subject matter of the problems makes the volume not only informative and valuable in the understanding of the fundamental principles but also useful in the solution of industrial problems. Nearly a hundred problems are presented in the following chapters: (1) Thermo-chemistry; (2) Dissociation of Gases, Law of Mass Action, Equilibrium and Temperature, Free Energy; (3) Electrolytic Dissociation, Solubility Product, Distribution Coefficient, Hydrolysis; (4) Reversible Cells, Gibbs-Helmholtz Equation, Free Energy and Temperature; *(5)* Speed of Reactions.

H. E. BENT

The Journal of the
American Chemical Society

VOL. 51 MAY, 1929 No. 5

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

STUDIES IN IODIMETRY. III. COPPER AS A STANDARD IN IODIMETRY

BY STEPHEN POPOFF, MARGARET JONES, CARL TUCKER AND W. W. BECKER

RECEIVED JANUARY 3, 1928 PUBLISHED MAY 6, 1929

The standardization of solutions in iodimetry has been studied extensively by many investigators. It has been shown by Popoff and Whitman[1] that potassium permanganate, potassium dichromate and potassium bromate can be used as independent standards for sodium thiosulfate solutions and that they all give practically the same value (within 0.05%) as that obtained when iodine is used as a standard.

It is usually considered that copper cannot serve as an independent standard for sodium thiosulfate solutions and therefore it is generally recommended that thiosulfate solutions be standardized against metallic copper under identically the same conditions that are to be used subsequently. It has been possible, however, to find conditions which give the same value (within 0.05%) when using copper and iodine as standards for sodium thiosulfate solutions. The foregoing was made possible by the use of an unquestionable, reliable and easily reproducible preliminary standard (iodine), by controlling the factors which influence the reactions so that variations were kept within 0.05%, and finally by the exclusive use of electrometric methods of determining the end-points.

The use of copper as a standard in iodimetry was first mentioned by de Haen[2] in 1854. Since 1854 many investigators have made a study of the causes of variations in the results obtained by standardizing the sodium thiosulfate solution against copper and against pure iodine. The larger deviations have been attributed to various causes.

The object of the present investigation was to determine the factors which influence the reaction between copper solutions and potassium iodide and thus to enable us to place copper as an independent standard in iodimetry.

---

[1] Popoff and Whitman, THIS JOURNAL, 47,2259 (1925).

[2] De Haen, Ann., 91, 237 (1854).

Materials

Iodine.—Best quality iodine was resublimed once from potassium iodide and twice alone.

Sodium Thiosulfate.—C. P. quality sodium thiosulfate crystals were placed in a large bottle, through the stopper of which a glass tube was connected to the condenser of an all-glass water still and redistilled water was distilled over into the bottle until the solution was approximately 0.1 N. The normality of this solution did not change for over three weeks.

Copper Sulfate.—Analyzed C. P. cupric sulfate was twice recrystallized and a 0.1 N solution was prepared using redistilled water.

Copper.—Pure electrolytic copper was employed. This metal was prepared by the method given on p. 1305.

Potassium Iodide.—A solution of Mallinckrodt's reagent quality potassium iodide was employed which gave no color to phenolphthalein and which contained no iodate.

Water.—The ordinary laboratory distilled water was redistilled in the presence of potassium permanganate in an all-glass apparatus.

Experimental Procedure

The easiest approach to the solution of the problem at hand consisted in the study of the various factors which determine the reaction between a copper sulfate solution and potassium iodide. If these were determined beforehand, it would be an easy matter to decide whether or not copper can serve as an independent standard for sodium thiosulfate solutions.

The factors which may determine the extent and kind of reaction are: (1) concentration of potassium iodide, (2) kind and concentration of acid, (3) cuprous iodide, (4) order of addition of reagents, (5) time of standing and (6) the presence of salts.

In order to study the foregoing factors, approximately 0.1 N solutions of copper sulfate and sodium thiosulfate were prepared and kept in bottles which were painted with black auto enamel. The reagents were added very slowly (about 15 cc. per minute) and with constant stirring whenever reactions were taking place. The end-point was determined electrometrically. The end-point was calculated by the simple process of interpolation described formerly.

Practically all of the determinations were made by using weight burets. The concentrations of all the solutions are expressed in the final volume, which was 160 cc. in all cases. The total time of each titration was about fifteen minutes. The copper sulfate was added from an especially made weight pipet. In all cases the volumes of the copper sulfate and the sodium thiosulfate solutions employed were about 35 to 38 cc. The numerical values given represent the averages of at least two determinations which did not differ by more than 0.05 of a per cent. Unless otherwise stated the copper sulfate solution was added to the potassium iodide solution.

1. Effect of the Concentration of Potassium Iodide.—The concentration of potassium iodide was varied from 2 to 24%. These concentrations do not allow for the iodide ion used up in the reaction. Table I shows the influence of the concentration of potassium iodide in the reaction between copper sulfate and potassium iodide in neutral solution. In all cases the iodide was added to the copper solution. The ratios are weight ratios of sodium thiosulfate solution to copper sulfate solution.

TABLE I

THE EFFECT OF CONCENTRATION OF POTASSIUM IODIDE

Concn. of KI, %	2	4	6	8	12
Weight ratios	1.0926	1.0935	1.0932	1.0928	1.0936

Up to 12% of potassium iodide the effect of increasing the concentration of potassium iodide is negligible. The lowest result obtained when 2% potassium iodide was used is no doubt due to loss of iodine, as in the final volume there was not 2% of potassium iodide present. When sufficient potassium iodide was present to dissolve the cuprous iodide completely, the weight ratio was increased by about 0.2%. The latter may be due to the oxidation of the cuprous ion to cupric by the air with the subsequent liberation of more iodine. It is possible, however, that Bray and MacKay's[3] suggestion that cuprous iodide adsorbs iodine is correct.

2. Effect of Kind and Concentration of Acid.—In order to determine the effect of acid on the reaction, the concentration of potassium iodide was kept constant at 4% and the reactions were made in neutral, 0.1 M sulfuric acid and 0.4 M acetic acid solutions. The reactions were carried out in the dark in order to prevent oxidation of the iodide ion by the air. The results obtained are recorded in Table II.

TABLE II

KIND AND CONCENTRATION OF ACID

Acid	Neutral	0.1 M sulfuric	0.4 M acetic
Ratios	1.0934	1.0959	1.0942

Evidently acid increases the amount of iodine set free. This may be due either to the oxidation of the iodide ion by the air, or to the oxidation of the cuprous ion to cupric (by the air) with the subsequent reaction with the iodide ion to form iodine. The presence of acid will no doubt increase the above oxidation. Since, however, it has been shown in previous investigations that the former does not take place in diffused light, the increase of the iodine set free may be due entirely to the oxidation of the cuprous ion to the cupric. Cuprous salts, especially the chloride and bromide, are well-known oxygen carriers in acid solutions.

Evidently the hydrogen-ion concentration is a decided factor, as the iodine set free is greater with sulfuric acid than with acetic acid. It is advisable, therefore, to keep the actual acidity as low as possible. The results obtained appear to differ from those reported by others. Bray and MacKay[3] find sulfuric acid objectionable but not acetic acid. Peters[4] finds that a small concentration of sulfuric acid or a large concentration of acetic acid can be employed without any effect.

3. The Effect of Cuprous Iodide.—In order to determine the effect

---

[3] Bray and MacKay, THIS JOURNAL, 32, 1199 (1910).

[4] Peters, *ibid.*, 34, 422 (1912).

of cuprous iodide, it was found necessary to prepare cuprous iodide and observe its effect upon the sodium thiosulfate–iodine reaction. The cuprous iodide was prepared by the addition of copper sulfate solution to potassium iodide solution. The cuprous iodide was washed with dilute potassium iodide solution (making use of the centrifuge) until practically free from iodine. The amount of iodine that remained in the cuprous iodide was determined by electrometric titration with sodium thiosulfate and the volume of thiosulfate required was subtracted from the total volume of thiosulfate in the subsequent titrations. Experiments were performed in which the effect of cuprous iodide on the thiosulfate–iodine reaction in the presence of 4% potassium iodide in neutral and in acid solution was determined. The results are given in Table III.

TABLE III

EFFECT OF CUPROUS IODIDE ON THIOSULFATE–IODINE REACTION

	Neutral, no CuI	Neutral + CuI	0.1 M H_2SO_4 + CuI	0.4 *M* HAc + CuI
Series I	0.9916	0.9917	....	....
Series II	.9905	....	0.9945	0.9930

From the foregoing results it may be concluded that cuprous iodide has no effect on the thiosulfate–iodine reaction in neutral solutions containing 4% of potassium iodide. In acid solutions, however, the effect is appreciable. It is advisable, therefore, to keep the solutions in titrations involving cupric salts and iodide ions as nearly neutral as possible. The effect of acetic acid seems to be much greater than that shown in Table II. This may be due to the fact that it was almost physically impossible to duplicate the experimental conditions.

4. Order of Addition of **Reagents.**—It was found that the order of addition of the reagents (when using 4% potassium iodide) made practically no difference, as the values obtained were 1.0935 and 1.0933.

5. **Time** of Standing.—In the dichromate-ion–iodine-ion–hydrogen-ion reaction it is necessary to let the reaction proceed for ten minutes before sodium thiosulfate is added. The effect of time of standing with the cupric-ion–iodide-ion reaction was determined using 4% potassium iodide. Table IV gives the results obtained.

TABLE IV

EFFECT OF TIME OF STANDING

	Weight ratio
Titrated immediately	1.0935
Standing for 10 min. before beginning titration	1.0934
Standing for 10 min. just before the end-point	1.0935

Evidently, under the conditions employed, the reaction between copper sulfate and potassium iodide goes to completion immediately and no time of standing is necessary.

6. The Presence of Salts.—The effect of the presence of salts was not determined. According to former investigators, potassium sulfate or salts in general decrease the amount of liberated iodine. It was deemed advisable, therefore, to keep the concentration of salts as small as possible in the standardization of the sodium thiosulfate solution by metallic copper.

The Determination of the Concentration of the Copper Sulfate Solution

From the study of the effect of the various factors in the copper sulfate–potassium iodide reaction, it was found necessary to perform the reaction in a solution which was as nearly neutral as possible and in the absence of salts. In order that these conditions might be rigidly maintained, a 0.1 *N* solution of copper sulfate was prepared and its concentration determined accurately by electrolysis. Former studies on the electrolytic determination of copper in this Laboratory by Tucker[5] were of special value.

The Electrolytic Determination of Copper.—A rotating platinum anode and copper gauze cathode served as the electrodes. A current of 1.5 amperes was used. The electrolysis was made to proceed until no positive test was obtained by haemotoxylin. The use of haemotoxylin as a test for copper was first introduced by Bradley;[6] however, no specific directions are given by former investigators. The test as finally employed was as follows.

About 2 cc. of the solution (after electrolysis had proceeded for about forty minutes) was placed in a small porcelain crucible. Two or three drops of the haemotoxylin indicator were added and then enough solid sodium carbonate to produce a red color. Finally, a saturated solution of sodium bisulfite was added dropwise until the red color disappeared. If copper were present, a blue color remained. A decided positive test for copper was obtained from a solution which contained 0.06 mg. of copper in 200 cc. of solution. If 0.06 mg. of copper still remained in solution the error would be about 6 parts in 30,000 or 0.02%. In this connection it may be of interest to state that the potassium ferrocyanide spot-plate test, as ordinarily used, is hardly sensitive enough as there can be as much as one mg. of copper without detection. Again, the method7 of adding more water to the electrolysis solution and observing whether or not any copper is deposited on the freshly exposed platinum surface of the cathode, cannot be considered a sensitive test for copper as we have not been able to observe any deposit of copper when there was 0.5 mg. of copper in 200 cc. of solution. Again, the method employed by Quisumbing and Thomas[7] of withdrawing the cathode is open to very serious objections, as is shown by the following experiments.

Solutions containing varying concentration of acids per 200 cc. were prepared. These were placed in the electrolysis apparatus and the weight of the cathode before and after withdrawal was determined. The current was left on and the cathode was quickly withdrawn and plunged into distilled water. This method will be called the "short cut" in order to contrast it with the "siphon" method, in which the electrolysis solution was continually being siphoned off and distilled water added so as to keep the solution over the cathode. The latter process is continued until the ammeter showed very little or no current (this required about 2 liters of water). Table V gives the results obtained.

---

[5] Tucker, Iowa "Thesis," 1924.

[6] Bradley, Chem. News, 94, 189 (1904).

[7] Quisumbing and Thomas, This Journal, 43, 1503 (1921).

TABLE V

LOSS OF COPPER USING THE "SHORT CUT" AND "SIPHON" METHODS OF WITHDRAWING THE CATHODE

Vol. of concd. acids, cc.	2, nitric	0.3, nitric	2, sulfuric	0.3, sulfuric
"Short cut" loss, mg.	1.3	0.3	1.8	0.8
"Siphon" loss, mg.	0	0	0	0

It can be seen readily that even at a concentration of 0.3 cc. of concd. nitric acid there is a loss of 0.3 mg. by the "short cut" method, as compared with no loss by the "siphon" method even when 2 cc. of concd. sulfuric acid were employed.

Strangely enough no one except Fales[8] has considered the solubility of the platinum anode in the electrolytic determination of copper. The solubility of platinum serving as the anode is not negligible and amounts to about 0.2 mg. when 2 cc. of concd. sulfuric acid and 1 cc. of concd. nitric acid per 200 cc. are employed. It must be stated, however, that Fales' suggestion of weighing the cathode after the deposition (not before) is complete, dissolving the cathode deposit and weighing the platinum electrode will hardly allow for the solvent action of the platinum anode. Certainly no platinum is present in the solution just as electrolysis is started. Any platinum that dissolves during the electrolysis will be deposited over the copper and it will be removed on dissolving the copper. It was ascertained that a mixture of nitric and sulfuric acids present to the extent of 0.15 cc. of each or 0.3 cc. of sulfuric acid only, will not exert solvent action on the platinum anode. In subsequent determinations these concentrations of acids were employed.

Although the haemotoxylin test for copper was negative, nevertheless it was deemed necessary to make absolutely certain that no appreciable amount of copper was left in the two liters of the "wash" solution There-fore the entire solution was evaporated to dryness. A few drops of nitric acid was added, the solution neutralized with ammonium hydroxide and then acidified with sulfuric acid. At the same time about two liters of water were evaporated and the residue (if any) treated in similar fashion. Potassium iodide was added to these solutions. Both solutions required only one drop of sodium thiosulfate to pass the electrometric end-point. It is believed that the foregoing tests show conclusively that the deposition of copper, as performed, is practically complete, especially since haemotoxylin gave no test for copper after the "wash" solution was evaporated to about two cubic centimeters.

Table VI gives the results obtained for the concentration of copper in the copper sulfate solution which was employed for the standardization of the sodium thiosulfate solution.

---

[8] Pales, "Inorganic Quantitative Analysis," Century Book Co., New York, 1925, p. 342.

TABLE VI

THE CONCENTRATION OF THE COPPER SULFATE SOLUTION

Series I. 0.15 cc. of HNO_3 + 0.15 cc. of H_2SO_4

	1	2	3	4
Wt. of $CuSO_4$ soln., g.	54.486	52.417	53.158	49.893
Wt. of Cu deposited, g.	0.3365	0.3235	0.3281	0.3052
Cu per g. of $CuSO_4$ soln., g.	0.006174	0.006171	0 006172	0.006177

Series II. 0.30 cc. of H_2SO_4

	5	6	7
Wt. of $CuSO_4$ soln., g.	50.892	50.655	50.603
Wt. of Cu deposited, g.	0.3141	0.3127	0.3125
Cu per g. of $CuSO_4$ soln., g.	0.006172	0.006173	0.006175

Average of Series I (excluding No. 4) = 0.006172
Average of Series II = 0.006173
Average of all values = 0.006173

The Standardization of Sodium Thiosulfate

Since pure elementary iodine is considered to be the best standard for sodium thiosulfate solutions, the sodium thiosulfate was standardized against pure iodine according to the method of Popoff and Whitman[1] and the results were compared with the values obtained when using the standard copper sulfate solutions and pure copper.

The Iodine Method.—The special apparatus described by Popoff and Whitman was employed. The final volume was 160 cc. and 4% of potassium iodide was used.

The Copper Sulfate Method.—The copper sulfate solution was added to a potassium iodide solution containing 4% of potassium iodide in the final volume of 160 cc.

The Copper Method.—Pure electrolytic copper was prepared and used in this determination. To prepare the pure copper, copper sulfate was recrystallized several times and an acidified solution of this salt was used in the electrolysis. A copper foil was employed as the cathode for the preparation of the electrolytic copper. It was a comparatively easy matter to remove the copper from the copper foil. The attempt to use aluminum foil failed as the electrolytic copper seemed to be contaminated with aluminum.

About 0.24 g. of copper was dissolved in 8 cc. of 6 M nitric acid. The solution was evaporated on the steam-bath until on cooling it would completely solidify. The residue was dissolved in about 20 cc. of water and dilute sodium hydroxide solution added until a permanent precipitate was just formed. Now 8 M acetic acid was introduced until the precipitate completely dissolved and then about four drops in excess. The solution was diluted to about 100 cc. with water and enough potassium iodide was added so that in the final volume of 160 cc. there would be 4% potassium iodide. If a sufficient amount of acetic acid was added to make the solution 0.4 M as directed by Fales, the error was increased by about 0.1%.

In all of the experimental work the potassium iodide was a 50% solution (by volume) and it was added very slowly with constant stirring (by an electric motor).

The copper sulfate solution, as well as the sodium thiosulfate solution, was weighed and the results given in Table VII are calculated on the basis of 1000 g. of sodium thiosulfate solution.

TABLE VII

THE NORMALITY OF THE SODIUM THIOSULFATE SOLUTION

Standard	Series	Normality	Diff. comp. to I_2, %	Series	Normality	Diff. comp. to I_2, %
Iodine	I	0.08880	..	I	0.00880	..
$CuSO_4$	I	0.08881	0.01	II	0.08883	0.03
Cu	I	0.08881	0.01	II	0.08881	0.01

No attempt will be made at this time to explain why previous workers were not able to make the standardization of a thiosulfate solution by copper check with other standards, because an explanation is not possible when all the factors are not known. One may venture stating that the standards and probably the conditions employed by former investigators were not ideal.

Summary

1. (a) From the study of the reaction between copper sulfate and potassium iodide, it was found that a change of concentration of the latter from 4 to 12% in neutral solutions had no effect on the thiosulfate–copper sulfate ratio.

(b) In the presence of 0.1 M sulfuric acid and 4% potassium iodide the thiosulfate–copper sulfate ratio is increased by about 0.2% and in the presence of 0.4 M acetic acid by 0.08%.

(c) The order of addition of the reagents makes no difference in neutral solutions when 4% potassium iodide is used.

(d) Time of standing (ten minutes) has no effect in the presence of 4% potassium iodide.

2. Cuprous iodide has no effect on the thiosulfate–iodine ratio in the presence of 4% potassium iodide and in neutral solutions. In acid solutions it causes an increase in the ratio.

3. Some glaring errors are pointed out in the electrolytic determination of copper. It is recommended that the concentration of acid be kept low and that practically all of the acid be removed before the copper cathode is taken from the solution. A very sensitive test for copper is used.

4. It is now possible to use either copper sulfate solution or pure copper as an independent standard in iodimetry provided the salt and the acid concentration are kept very small.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

STUDIES IN IODIMETRY. IV. POTASSIUM PERMANGANATE AS A STANDARD IN IODIMETRY

BY STEPHEN POPOFF AND ADOLF H. KUNZ

RECEIVED JANUARY 6, 1928 PUBLISHED MAY 6, 1929

Although in a former article[1] it has been shown that potassium permanganate can be used as an independent standard in iodimetry, there were a number of factors which necessitated further study, especially in view of some helpful suggestions by Dr. W. C. Bray. In the former investigation volume burets were employed and it seemed that differences of 0.05% could well be attributed to experimental errors. Weight burets were used in the present investigation in order to reduce errors to a minimum.

Winther[2] has shown that in acid solution the rate at which oxygen reacts with iodide ion in the dark increases as iodine is liberated and that it proceeds much more rapidly in the light. It is true that the thiosulfate–permanganate ratio in **0.1** *M* sulfuric acid is larger when 6% iodide is used than with 2%. However, when iodine solution is titrated under the same conditions no difference in the thiosulfate–iodine ratio is obtained.[3] This indicates that the difference must be due to some other factors.

Effect of Salts.—Since in the titration of the iodine set free by permanganate there are manganous and potassium salts present, the influence of these salts on the thiosulfate–iodine reaction was studied. Table I shows that manganous sulfate and potassium sulfate in 6% potassium iodide and 0.1 M sulfuric acid solution and with ten minutes' standing before titration have no effect on the thiosulfate–iodine reaction. The amount of these salts added was that equivalent to 40 cc. of **0.1** *N* potassium permanganate.

TABLE I

EFFECT OF POTASSIUM AND MANGANOUS SALTS

	Wt. ratio		Wt. ratio
No salts present	1.0701	Salts present	1.0704
No salts present	1.0702	Salts present	1.0702

Effect of Concentration of Iodide, Acid and Light.—It seemed desirable to show that in the thiosulfate–iodine reaction up to 6% potassium iodide and **0.1** M sulfuric acid can be used together with ten minutes standing without producing any appreciable change in the thiosulfate–iodine weight ratio, provided, of course, the titrations are carried out in the dark. Table II bears out this statement. In this and subsequent tables the concentrations given are at the end of the titrations. Where

---

[1] Popoff and Whitman, THIS JOURNAL, 47, 2259 (1925).

[2] Winther, *Z. physik.* Chem., 108, 236 (1924); 113, 274 (1924).

[3] See ref. 1, p. 2270.

duplicate results are not given, the values were obtained from two or more determinations in which the maximum variation was 0.05%.

TABLE II

EFFECT OF CONCENTRATION OF IODIDE, ACID AND LIGHT

Potassium iodide, %	2	2	6	
Acid	None	None	0.1 M sulfuric	
Time of standing	None	None	Ten minutes	
Wt. ratio in light	1.0688	1.0686	1.0701	1.0702
Wt. ratio in dark	1.0689	1.0693	1.0690	1.0691

The light used in the experiments with 6% potassium iodide was artificial light from four 100-watt bulbs in a room 18' X 15' × 13'. Evidently light from such an electric source cannot be substituted for diffused light. In subsequent experiments red light furnished the necessary illumination.

Winther[2] showed that in the light oxidation of iodide by blowing air through the solution requires a thirty-minute induction period and that the speed of the reaction is increased by the presence of a very small amount of iodine. In our experiments air is not blown through the solutions, there are about 40 cc. of 0.1 N iodine solution present, the time of titration is at most twenty-five minutes and the experiments are performed in the dark. Therefore, the conditions under which Winther performed his experiments are widely different and no appreciable oxidation of the iodide ion takes place under the conditions recommended in our work in iodimetry.

Effect of Rate and Method of Introducing Permanganate.—A study was made of the effect on the thiosulfate–permanganate ratio of introducing the permanganate above and below the surface of the acidified solution of potassium iodide, the acid concentration being 0.1 M sulfuric acid. The stirring during the addition of the permanganate was not done by means of an electric motor as in the experiments (open vessel) given in Table V. The diierence between the results given in Tables III and V emphasizes

TABLE III

EFFECT OF RATE AND METHOD OF INTRODUCING PERMANGANATE

% KI	Time of standing	Rate of addition	Method of addition	Thiosul.-perman. wt. ratio
6	None	5 minutes	Above	1.0836
6	None	5 minutes	Above	1.0838
6	10 minutes	5 minutes	Above	1.0836
6	10 minutes	5 minutes	Above	1.0832
6	10 minutes	5 minutes	Below	1.0836
6	10 minutes	5 minutes	Below	1.0838
6	10 minutes	1 minute	Above	1.0836
6	10 minutes	5 minutes	Above	1.0832
2	None	1 minute	Below	1.0817
2	None	1 minute	Below	1.0818
2	None	1 minute	Above	1.0798
2	None	1 minute	Above	1.0800

the necessity of using 6% rather than 2% potassium iodide. The results are given in Table III.

These results show that neither the rate nor mode of addition (within certain limits) of the permanganate has any effect when 6% potassium iodide is used. When 2% iodide is used the weight ratio is greater when the permanganate is added below the surface. Evidently 6% potassium iodide is to be preferred.

In the former paper we quoted incorrectly that Bray and MacKay[4] claimed that the reaction between the permanganate and iodide is slow, hence the necessity of using 6% potassium iodide and ten minutes' standing. This contention, however, must be abandoned in view of the more precise data given in Table III. The former results may be attributed to the failure to exclude light from artificial source (see Table II).

Effect of Alkali.—While it is generally known that the potassium iodide used in most work in iodimetry must be practically free from alkali, yet labels of many analyzed "c. p." samples of potassium iodide do not specify the alkalinity. It is very likely that some of the workers who have recommended the use of acid solutions, when standardizing thiosulfate solutions with iodine, had used slightly alkaline iodide without being aware of the presence of the alkali. Table IV shows the effect of using a "c. p." potassium iodide (analysis of which showed alkali) compared to another not containing alkali.

TABLE IV

EFFECT OF ALKALI IN POTASSIUM IODIDE

% KI	Acid	Thiosulfate–iodine weight ratio Alk. iodide	Non-alk. iodide
2	0.1 *M* H_2SO_4	1.0695	0.9522
2	0.1 M H_2SO_4	1.0695	.9524
2	No acid	1.0672	.9523
2	No acid	1.0669	.9524

It is recommended that the specifications for potassium iodide given by the Committee on Guaranteed Reagents[6] be followed rigidly.

Effect of Concentration of Potassium Iodide in Closed and Open Vessels.—It was further deemed advisable to study whether or not the large difference in the thiosulfate–permanganate ratios, when using 2 and 6% potassium iodide, is due to the fact that iodine is set free rapidly and that unless 6% iodide is employed iodine is lost by volatilization. In order to determine this, a special apparatus was constructed in which the formation and titration of practically all the iodine were performed in a closed vessel similar to the one previously used for weighing iodine.[6] The endpoint was then determined in a beaker. Not more than six drops was re-

---

[4] Bray and MacKay, THIS JOURNAL, 32, 1193 (1910).

[5] *Ind. Eng. Chem.*, 19, 648 (1927).

[6] See ref. 1, p. 2266.

quired to obtain the electrometric end-point. Table V gives the data obtained.

TABLE V

EFFECT OF CONCENTRATION OF POTASSIUM IODIDE IN CLOSED AND OPEN VESSELS

Potassium iodide, %	2	2	6	6
Vessel	Closed	Open	Closed	Open
Thiosul.-perman. wt. ratio	1.2155	1.2148	1.2173	1.2164

It can readily be seen that the difference between using 2 and 6% potassium iodide in the permanganate–iodide reaction is not due to loss of iodine in the former by volatilization. It must probably be attributed to the "loss of oxygen" by the permanganate while in the process of reduction. It is significant to note that the loss of iodine in 2 and 6% potassium iodide (when results in closed and open vessels are compared) is about the same.

The Weight Normality of Potassium Permanganate Solution.—In order to show that 6% potassium iodide must be employed in the permanganate method and no time of standing is necessary, the data of Table VI are presented. The standardization of potassium permanganate with sodium oxalate was carried out as recommended by McBride[7] (except that the end-point was determined electrometrically). In the standardization of the sodium thiosulfate by iodine, 2% potassium iodide was employed, while by potassium permanganate 6% of potassium iodide and 0.1 M sulfuric acid. All concentrations are referred to a final volume of 160 cc. About 40 cc. of solution was used and about 20 cc. of water was employed for washing the sides of the vessel just before the end-point.

TABLE VI

THE WEIGHT NORMALITY OF POTASSIUM PERMANGANATE SOLUTION[a]

Normality by sodium oxalate	1.0484
Normality by iodine and wt. ratio of thiosul.-permanganate	1.0483

[a] In all the experiments at least two duplicate determinations were made with a maximum variation of 0.05%.

Summary

1. It has been shown by using weight burets that in the thiosulfate–iodine reaction there is no appreciable oxidation of the iodide ion by the oxygen of the air in a solution containing 6% potassium iodide and 0.1 M sulfuric acid, even after standing for ten minutes, provided titrations are made in the dark.

2. Manganous and potassium sulfates in concentrations corresponding to 40 cc. of 0.1 N potassium permanganate have no effect under the conditions specified in 1.

3. Potassium iodide used in iodimetry must meet the specifications of the committee on guaranteed reagents in respect to alkalinity.

---

[7] McBride, THIS JOURNAL, 34,393 (1912).

4. Six per cent. potassium iodide must be employed when sodium thiosulfate solutions are standardized with potassium permanganate. Standing is not necessary. The acid concentration may be 0.1 M sulfuric.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. IV. PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

BY RUFUS D. REED AND JAMES R. WITHROW

RECEIVED JULY 16, 1928 PUBLISHED MAY 6, 1929

This paper is devoted to a study of the completeness of precipitation of zirconium by other phosphates. In testing for completeness of precipitation of potassium by zirconium sulfate it was found that this reagent also gave a precipitate with sodium cobaltic nitrite. Therefore, it became necessary to remove the zirconium before testing for potassium. As phosphates have been used for quantitatively determining zirconium and as Noyes and Bray[1] have shown that phosphates do not interfere with the detection of potassium by sodium cobaltic nitrite, the completeness of removal of zirconium by phosphates prior to testing for potassium was investigated.

The results indicated that a five-fold excess of ammonium phosphate, phosphoric acid or microcosmic salt in the presence of 0.344 molal sulfuric acid were all efficient in removing zirconium but that sodium phosphate was inefficient except when used in forty-fold excess. The presence of added acid was necessary.

Literature

Phosphates.—Sodium phosphate,[2] ammonium phosphate,[3] microcosmic salt[4] and phosphoric acid[5] have been used to determine zirconium quantitatively in the presence of sulfuric acid. Biltz and Mecklenburg[6] recommend the qualitative detection of zirconium by sodium phosphate in the presence of hydrochloric or nitric acid, as sulfuric acid slowed up the reaction.

Conditions for the Precipitation of Zirconium Phosphate.—Marden and Rich[2] recommend "a slight excess of sodium phosphate" in the presence of 10% sulfuric acid. Lundell and Knowles[3] recommend an excess of 10 to 100 times the calculated amount of ammonium phosphate in

---

[1] Noyes and Bray, THIS JOURNAL, **31,** 634 (1909).

[2] Marden and Rich, *J. Ind. Eng. Chem.*, *12*, *654* (1920).

[3] Lundell and Knowles, THIS JOURNAL, **41,** 1801 (1919).

[4] Steiger, *J. Washington Academy of Science*, 8, 637 (1908).

[5] Marden and Rich, Bureau of Mines, Bulletin No. 186, 75–77 (1921).

[6] Biltz and Mecklenburg, *Z. angew. Chem.*, *25*, 2110 (1912).

the presence of 2 to 20% tepid sulfuric acid. Less than 0.5% sulfuric acid caused the formation of basic zirconium phosphate. Noyes, Bray and Spear[7] found that an excess of sodium phosphate was needed to remove practically all of the zirconium from solution. Steiger[4] stated that the zirconium was completely removed by microcosmic salt except when the acidity was from 5 to 10% sulfuric acid. Marden and Rich investigated the yield of zirconium phosphate by precipitation with various phosphates and concluded[5] "that $(NH_4)_2HPO_4$, Na_2HPO_4 or H_3PO_4 gave equally good results." If one chooses results from their determinations given in the table, agreeing results are secured, but the average of their determinations of zirconium by sodium phosphate is less than the average of either the ammonium phosphate or phosphoric acid results.

While zirconium has been determined quantitatively by all four phosphates, their efficiency in removing zirconium completely in the presence of hydrochloric, nitric and sulfuric acids of varying concentrations was still subject to question. It was decided, therefore, to investigate the completeness of removal of zirconium by these phosphates.

Experimental

Reagents.—The zirconium sulfate solution contained **0.1134** g. of zirconium sulfate per cc. The approximate strengths of the acids were determined by specific gravity. The phosphates were analyzed for phosphate by the magnesium pyrophosphate method according to Treadwell and Hall.[8]

General Procedure.—To 1-cc. portions of zirconium sulfate solution in the presence of no added acid and also hydrochloric, nitric or sulfuric acid, a solution of either phosphoric acid, sodium phosphate, microcosmic salt or ammonium phosphate was added. After standing for two hours or overnight the solutions were filtered through closest grained filter paper and washed four times with cold water. Early experiments showed that if medium texture paper was used the zirconium phosphate would pass through the paper. To make any precipitate more noticeable, the filtrate and washings were concentrated upon a sand-bath to **10** or **20** cc. Then concentrated ammonium hydroxide was added to neutralize the acid. If the solution gave no deposit, it was warmed and allowed to stsnd to see if a tardy precipitate would form.

Sodium phosphate as a reagent for precipitation of zirconium was investigated more minutely than the others as it would not interfere with the detection of potassium after zirconium was removed. The efficiency of all four reagents is shown in the table.

Discussion

In Expts. 1 to 4 where no acid was added the precipitate settled slowly and filtered with difficulty. In Expts. 5 to 25 where acid was added the precipitate settled readily and filtered much more rapidly than where no acid was added. Evidently acid must be added to secure a proper

---

[7] Noyes, Bray and Spear, THIS JOURNAL, 30, 559–560 (1908).

[8] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1915, Vol. II, p. 474.

TABLE I

PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

Expt.	Added acid Kind	Added acid G.	Total vol., cc.	Ppt. calcd., P_2O_5	Calcd. factor as excess, P_2O_5	Test in filtrate for zirconium by NH_4OH Na_2HPO_4	H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$
1	None	....	50	0.5696	10.0	Ppt.	Ppt.	Ppt.	Sl. ppt.
2	None	....	200	2.2792	40	....	Clear No. ppt.	....	....
2a	None	....	50	2.2792	40.0	....	Few dark flocks	....	....
3	None	....	100	5.6980	100.0	....	Clear No ppt.	Sl. ppt.	....
4	None	....	200	1.1396	20.0	....	Dark ppt.	....	....
5	HCl	0.410	54	0.0929	1.33	Ppt.	....	....	....
6	HCl	.410	54	.0929	1.33	Ppt.	....	....	....
7	HCl	.373	50	.1139	2.00	Ppt.	....	....	....
8	HCl	9.325	50	.1139	2.00	Ppt.	....	....	....
9	HCl	0.373	50	.5696	10.00	Ppt.	Ppt.	Ppt.	Ppt.
10	HCl	1.230	152	2.0907	36.7	Sl. ppt. overnight	....	....	....
11	HCl	0.373	50	1.1396	20.0	....	Sl. ppt.	Sl. ppt.	Sl. if any ppt.
12	HCl	.373	50	2.8490	50.0	....	No ppt. clear	....	....
13	HNO_3	.358	50	0.2321	4.05	Sl. ppt. on standing	....	....	....
14	HNO_3	8.717	50	.2321	4.05	Ppt. on standing	....	....	....
15	HNO_3	4.3585	50	1.9658	32.4	Ppt. on standing	....	....	....
16	HNO_3	0.896	50	0.5696	10.0	Ppt. on standing	Sl. ppt.	Ppt.	Sl. ppt.
17	HNO_3	.8966	50	1.1396	20.0	....	Clear No ppt.	Clear No ppt.	Sl. if any ppt.
18	H_2SO_4	.1634	50	0.5405	9.48	....	....	....	Ppt. standing
19	H_2SO_4	.817	50	.2849	5.00		Cloudy	Ppt.	Clear No ppt.
20[a]	H_2SO_4	.817	50	.5696 .5405	10.0	Ppt. on standing	Sl. ppt.	Clear No ppt.	Clear No ppt.
21	H_2SO_4	1.634	50	.2849	5.0	....	Clear No ppt.	Clear No ppt.	Slight if any ppt.
22	H_2SO_4	1.6417	50	.4642	8.15	Ppt. on standing	....	....	....
23	H_2SO_4	1.634	50	.5698	10.0	....	Clear No ppt.	Clear No ppt.	Clear No ppt.
24	H_2SO_4	3.2324	100	.3215	40.05	No ppt.	....	....	....
25	H_2SO_4	8.17	50	.5718	10.0	....	....	Sl. cldy.	Clear No ppt.

[a] The amount of ammonium phosphate used in Expt. 20 was not 0.5696 g. of P_2O_5 as in the other three cases but 0.5405 g. of P_2O_5. All other conditions were the same.

physical condition of the precipitate. In Expts. 18 to 25, where sulfuric acid was present, the precipitate formed only after standing for a few seconds, while in all other cases, Expts. 1 to 17, where either none or hydrochloric or nitric acid was present, it formed as soon as any precipitant was added. This agreed with the observation of Biltz and Mecklenburg.[6]

In Expt. 5 the zirconium was precipitated from hot solution while in Expt. 6 the precipitation was made from solution at room temperature, all other conditions being equal. The bulk of precipitate was greater in the filtrate from 5 than from 6, possibly indicating that zirconium was more completely removed when precipitation was made at room temperature than from hot solution. All other precipitations were made at room temperature.

Effect of Added Acid.—In Expts. 5 to 12 where hydrochloric acid was present, only one condition—Expt. 12, 0.204 N hydrochloric acid—succeeded in removing all of the zirconium. An excess of 50 times the calculated amount of phosphoric acid was needed for this. Expts. 13–17, where 0.269 N nitric acid was present, indicated that in Expt. 17, 20 times the calculated needed amount of phosphoric acid, microcosmic salt or ammonium phosphate would remove all of the zirconium from solution. Expts. 18–25, in which sulfuric acid was present, indicated that either phosphoric acid, microcosmic salt or ammonium phosphate—Expts. 20, 21, 23—when used in excess of 5 to 10 times the calculated needed amount would remove all of the zirconium from solution in the presence of 0.817 g. (0.168 molal or 0.334 normal) to 1.634 g. (0.334 molal or 0.668 normal) of sulfuric acid per 50 cc. of solution. Expt. 25 showed that as much as 8.17 g. of sulfuric acid per 50 cc. of solution did not prevent the complete removal of zirconium by 10 times the calculated amount of ammonium phosphate. These results indicated that the presence of sulfuric acid, while retarding the appearance of a precipitate, was more beneficial than either hydrochloric or nitric acid in aiding the removal of zirconium by phosphates.

Efficiency of Various Phosphates.—Sodium phosphate—Expts. 19 to 23—was less efficient than phosphoric acid, microcosmic salt or ammonium phosphate in removing zirconium from solution. However, the amount of zirconium left in solution by sodium phosphate was very small and the precipitate of zirconium phosphate formed only after standing. The bulk of the deposits, in the ammonium phosphate column, marked "slight if any" amounted to but a few flakes which would be unweighable on ignition and might have been shreds of filter paper.

Summary

1. The efficiency of sodium phosphate, phosphoric acid, ammonium phosphate and microcosmic salt as precipitants for zirconium has been investigated and the last three were found to be equally efficient and more efficient than sodium phosphate. Even sodium phosphate removed practically all of the zirconium.

2. The phosphates were found most efficient in the presence of 0.344 to 0.668 N sulfuric acid and less efficient in the presence of 0.269 N nitric acid or 0.204 N hydrochloric acid.

3. Although record was found in the literature of the formation of

basic zirconium phosphate in the absence of added acid, no record was found indicating incompleteness of precipitation of zirconium under these conditions. Investigation showed that phosphates are not efficient in removing zirconium in the absence of added acid.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAPE TOWN]

THE SINGLE POTENTIAL OF THE COPPER ELECTRODE

BY EDGAR NEWBERY

RECEIVED JULY 20, 1928 PUBLISHED MAY 6, 1929

The determination of the normal single potential of a copper electrode has been attempted by many investigators with very discordant results and at the present time its value is not known with certainty within a possible error of 40 millivolts. This work was undertaken, therefore, with the object first of finding the reasons for the variation in the results obtained, and, second, if possible, of removing or circumventing the disturbing factors and determining the true value.

Possible sources of error or of variability of results are: (1) impurities in the electrode, (2) impurities in the electrolyte, (3) variations in the nature of the electrode surface, (4) changes in constitution of electrolyte during measurement, (5) chemical action between electrode and electrolyte producing any or all of the conditions (1) to (4).

1. Most investigators have exercised great care to ensure that the copper electrodes used were free from traces of other metals. Unfortunately one of the most dangerous impurities, hydrogen, which is very frequently present and has a profound potential-disturbing capacity, has been ignored. If two copper plates cut from the same sheet be immersed in dilute acid and a current passed for a few seconds, a potential difference of several millivolts is produced which may persist for several hours. By introducing a third electrode cut from the same sheet at the same time it may be shown that this potential change is mainly due to the cathode.

This cannot be due to deposition of copper on the cathode since the effect is quite unchanged if the three electrodes are placed in separate compartments connected only by narrow tubes.

Lewis and Lacey[1] used electrolytic copper sponge for the determination of the single potential of copper and this was undoubtedly contaminated with hydrogen.

Their attempt to show that occluded hydrogen was not taking part in the electrode process was very unconvincing. They found that the presence of 0.0005 M sulfuric acid in the solution had no effect upon the e.m.f.

---

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

If the hydrogen in the copper exists as unsaturated solid solution, as is probably the case, such a solution will show a single potential intermediate between that of pure copper and of a hydrogen electrode. The effect of change of H-ion concentration will, therefore, be much less than in the case of a hydrogen electrode. Also, the extremely small quantity of acid added by Lewis and Lacey, the buffer action of the salt present and the natural acidity of the copper sulfate solution due to hydrolysis (copper hydroxide being a weak base) all indicate that the change of H-ion concentration due to the addition of the acid must have been very small.

If more concentrated acid is used (say 0.05 M), the tendency for the copper to go into solution becomes marked and a considerable fall of potential is observed (5 or 6 millivolts) whether the electrode contains hydrogen or not. With an electrode containing hydrogen in very dilute acid, the two effects tend to balance each other.

Lewis and Lacey's experiment, therefore, fails to prove that the original single potential of the copper was not affected by the presence of hydrogen.

2. The precautions taken by most investigators with regard to the purity of the copper salts and the water used preclude the possibility of any serious errors from this source. Further, preliminary experiments showed that quite appreciable quantities of certain impurities—acid, iron salts, etc.—had very little effect upon the measured potentials.

3. It is remarkable that nearly all workers have been unanimous in ascribing the variations in measured single potentials of copper to variations in the nature of the surface.

Preliminary experiments were carried out in order to examine this effect. Various specimens of copper wire, sheet, ingot, etc., were subjected to the most drastic treatment—heating to near the melting point and cooling in ice water or very slowly in an electric furnace, drawing wire through dies, hammering out to thin plates, cleaning with several grades of emery or glass paper, polishing, burnishing, etc., but the results were entirely negative. In no case could any change of potential be definitely ascribed to mechanical conditions. It is evident, therefore, that this effect has been greatly overestimated.

Getman[2] investigated this effect and came to a similar conclusion. Unfortunately, however, he rendered his results of doubtful value by polishing his samples with emery cloth after each treatment, thus destroying to some extent the surface he had been preparing. In the above work all cleaning was done before other treatment, the formation of oxide films during heating being avoided by carrying this out in a vacuum, except in the case where sudden cooling was required. In the latter case the oxide film was removed by scraping with a steel knife and is thus open to criticism, but the remaining cases are sufficient to indicate that the theory of surface strains is

---

[2] Getman, *Trans. Am. Electrochem. Soc.*, **26,** 67(1914).

inadequate to explain the large changes of single potential observed when copper is placed in a solution of one of its salts or when different forms of copper (massive, sponge, powder, amalgam, etc.) are used.

On the other hand, the nature of the surface certainly affects the speed of the reaction which occurs between electrode and electrolyte (see under 5). If, therefore, thirty minutes be allowed in each case (as was done by Getman) for this reaction to proceed, differences of potential may well be observed, but these are not true normal potentials.

The maximum potential differences found by Method C, described later, between dead, soft and hard hammered copper and between brightly polished and very rough surfaces were of the order of one millivolt, whereas the values found by Getman vary by 30 millivolts in 0.01 M solution and by 200 millivolts in 0.001 *M* solution.

4. The stability of copper sulfate solutions is open to question. It is frequently observed that a bottle of the solution standing for some months in the laboratory deposits a pale blue precipitate. O'Sullivan[3] observed a marked drift of the potential of a quinhydrone electrode in neutral copper sulfate solution amounting to over 20 millivolts in seven days, but accounted for this by the reducing action of the quinhydrone on the copper sulfate. He found that no change was observable in copper sulfate solution which had been kept for a month. From experiments carried out in connection with the present work, it appears probable that if he had used a solution three to six months old, a change would have been observed.

A sample of 0.5 M copper sulfate which had been kept in a stoppered measuring flask for three months was compared with a fresh solution by measuring the single potential of a clean copper rod against a mercurous sulfate electrode first in the old solution and then in the new. The rod was cleaned before each immersion and rotated during measurements and a definite difference of potential of 2 to 4 millivolts was observed as a result of about 24 measurements. This would appear to involve a change of the order of 17 to 37% in the concentration of the copper ions in solution. A similar sample of solution which had been kept in a partly filled stoppered bottle for nearly a year and which showed a visible precipitate, gave a value of the single potential of copper 20 millivolts lower than that in a fresh solution. This would imply a reduction of the copper-ion concentration to one-fifth of that in a fresh solution—a very improbable effect. It is possible that crystalline copper sulfate may consist largely of a complex cupri-sulfuric acid and that the real concentration of copper ions in solution is very small and easily disturbed without producing any marked visible effect in the solution as a whole. Possibly also the solution may tend to decompose with the formation of cuprous salt which remains in colloidal solution, and alkali dissolved from the glass container may affect

---

[3] O'Sullivan, *Trans. Faraday Soc.*, **23**, 52 (1927).

either of these conditions. In any case, the action under ordinary conditions is a very slow one and cannot account for the rapid changes of 2 millivolts in two minutes frequently observed when a clean copper electrode is placed in old or fresh solution.

5. In order to ascertain whether the electrolyte reacted with the electrode, small copper rods or strips of foil were prepared in various ways and placed in solutions of cupric sulfate, chloride, nitrate and acetate. In every case visible chemical action occurred and the electrodes were coated with basic salts. In some cases, notably with rough electrodes in chloride solutions, the effect was visible after a few seconds' immersion, in other cases it was much slower. A highly polished strip of foil completely covered with a half molar solution of pure copper sulfate and enclosed in a weighing bottle containing only a small quantity of air was not visibly affected during the first twenty-four hours. After four weeks a fairly thick, hard-red deposit was formed on the copper near the surface of the liquid and along minute scratches left by the polishing, but most of the surface was still bright and untarnished. The admission of air materially hastened the formation of further deposit.

In some solutions, crusts a millimeter thick containing visible faces of dark green crystals were formed in less than a week.

Since an invisible film of no more than molecular thickness may profoundly affect the single potential of the metal, it is evident that this action is the main source of all the difficulties experienced in determining the single potential of copper.

The following experiments were carried out, therefore, with a view to eliminate the effect of this film.

Experimental

(A) The first method of attack consisted in an attempt to determine the single potential of the copper immediately after the passage of a very small current either depositing or dissolving copper from an electrode in a half molar solution of the sulfate. For this purpose the rotating commutator apparatus previously used for overvoltage measurements was employed.[4] A Tinsley vernier potentiometer reading to five significant figures with no slide wire and a galvanometer reading to 10^{-9} amp. were used. The subsidiary electrode was a sheet of pure copper and the standard electrode was mercurous sulfate in half molar sulfuric acid.

When the experimental electrode is made the cathode, pure copper is deposited on it and the single potential of this was measured at such a short interval after interrupting the current that the objectionable film of basic salt has no time to form. The deposited copper, however, always contains hydrogen and the single potential will, therefore, always be too low (negative).

On the other hand, when the experimental electrode is the anode, small quantities of metal will be removed continuously from the surface, thus hindering the formation of a basic film but at the same time oxygen or some oxidizing agent is formed on the surface and the measured single potential will be too high (positive).

---

[4] Newbery, *J. Chem. Soc.*, **105,** 2420 **(1914).**

It was hoped that an extrapolation to zero current would eliminate **both** of these errors. At the same time errors due to local changes of concentration were eliminated by stirring the liquid by means of a small spiral glass stirrer revolving rapidly in front of the electrode. At first currents of *a* few micro-amperes were tried, but the single potentials observed were very erratic and indefinite. When heavier currents up to 12 milliamperes per sq. cm. were applied, more consistent results were obtained and these are illustrated by the curve shown in Fig. 1, which gives the average values obtained in four complete series of observations. In this curve ordinates represent the single potential in volts (assuming that of the normal mercurous sulfate electrode to be 0.968 volt at 20°) and abscissas the current density in milliamperes per sq. cm.

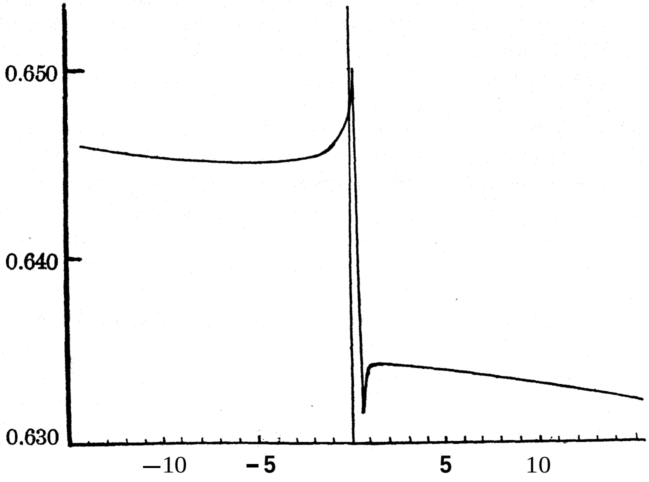


Fig. 1.

It is evident that extrapolation to zero current is quite out of the question with a curve such as this, where the two branches of the curve are pointing in opposite directions instead of approaching each other near the zero line as might have been expected. It is, however, of considerable interest as showing that the production of hydrides or other reducing bodies at the cathode and of oxides or other oxidizing bodies at the anode occurs even at extremely low current densities. In fact, the single potential of the electrode depends greatly upon its previous history for some time past. An attempt was next made to bring the two arms of this curve together by constructing a triple four-part commutator which gave the following cycle: (1) current applied, test electrode cathode; (2) current broken, test electrode connected to potentiometer; (3) current applied, test electrode anode; (4) current broken, test electrode connected to potentiometer. When the commutator gave about twenty complete cycles per second, steady readings were obtained on the potentiometer at all current densities and it was found that these readings were almost unaffected by changes of current density. Nevertheless, the original slow drift of potential again became evident, so it appeared that this treatment could not succeed in preventing formation of films of basic salt.

The addition of sulfuric acid up to a concentration equal to that of the copper salt was next tried with both of the preceding methods but no greater consistency was observed.

(B) The electrochemical methods outlined above having failed to prevent the formation of the basic film, purely chemical methods were next tried. When a strongly acid solution of cupric chloride is treated with metallic copper in excess, the remaining copper appears clean and fairly bright. An attempt was therefore made to prepare a cuprous chloride electrode after the style of the calomel electrode. The above solution was precipitated by the addition of air-free water and washed with normal potassium chloride solution. It was found that the pure white precipitate acquired a yellow stain as soon as the acidity fell below a certain limit even in complete absence of free oxygen, evidently due to hydrolysis of the cuprous chloride. The stain was very slight and the following cell was therefore made up: $Cu | CuCl_2 | M KCl | Hg_2Cl_2 | Hg$. An average value of 0.1385 volt at 20° was obtained, which was fairly constant for two hours, but this rose to over 0.14 volt in forty-eight hours. This change of potential cannot be due to oxidation of the cuprous chloride since that would have lowered the e.m.f. of the cell. Hence, it must be concluded that chemical action is proceeding between electrode and electrolyte. On dismantling the cell, the copper electrode was found to be coated with a dark brown substance. Other relatively insoluble copper salts were tried with similar results and this line of attack was therefore abandoned.

(C) Since chemical and electrochemical methods failed to produce the desired effect, purely mechanical methods were again resorted to. Very rapid stirring of the electrolyte and very rapid rotation of the electrode were found only to retard the rapid change of potential of copper in various solutions of cupric salts. Mechanical cleaning of the electrode while immersed in the electrolyte would be difficult and results obtained would be open to considerable doubts as to the effect of such cleaning on the equilibrium between electrode and its ions. The electrode was therefore arranged in a rotating holder so that it could be easily and rapidly cleaned, and immersed in the electrolyte immediately after. The glass tube leading from a mercurous sulfate electrode in half molar copper sulfate was arranged alongside the freshly cleaned and still rotating copper electrode and immersion of both effected by quickly raising a beaker containing half molar copper sulfate previously placed below the electrodes. Before this was done the electrodes were connected to the potentiometer, which was set as near as possible to the point expected. Raising the beaker then completed the potentiometer circuit and the first direction of movement of the galvanometer was noted. Continued repetition of this process, the electrode being washed, dried and cleaned each time, finally gave a limiting value which could be reproduced with different electrodes repeatedly within a few tenths of a millivolt. The electrodes were in the form of small circular rods or thick wires with flat ends, the upper portions being covered with hard sealing wax; the cleaning was effected with No. 000 emery paper or rouge paper. The final value obtained for the cell $Cu | 0.5\ M\ CuSO_4 | Hg_2SO_4 | Hg$ was 0.3630 ± 0.0005 volt at 20°.

Nielsen and Brown[6] have carried out a series of careful determinations using a two-phase copper amalgam as a standard copper electrode. It appeared of interest, therefore, to compare the above result with such an amalgam electrode. Three samples of copper amalgam were prepared by the electrolysis of acidified copper sulfate solution with a mercury cathode, and after thorough washing and heating to destroy any hydride and expel any adsorbed hydrogen present, were used in the above cell to replace the copper electrode. All three samples gave the value 0.3633 ± 0.0003 volt at 20°. We thus arrive at the conclusion that within the limits of experimental error the single potentials of pure copper and of two-phase copper amalgam are identical. Nielsen and Brown's claims for the two-phase

---

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

amalgam as a standard form of copper are therefore justified in a wider sense than the authors appeared to expect. At first sight it seems remarkable that the presence of a large quantity of mercury should have absolutely no effect upon the single potential of copper but the case is not without parallel. In the case of the hydrogen electrode, the single potential of the base metal—platinum, palladium, etc.—is completely submerged and that of the dissolved and dissociated atomic hydrogen alone determines the observed values.

The action of the mercury in checking the influence of basic films on copper appears to be similar to its action on aluminum, where the softening of the underlying metal allows of easy fracture of the oxide film with consequent exposure of the metal. Formation of a film is not entirely prevented by the mercury in the case of copper amalgam, as may be shown by allowing an amalgam electrode to stand under pure copper sulfate for some hours. A steady drift of potential occurs similar to that in the case of pure copper but very much slower. After a few days a red crystalline deposit appears on the amalgam but the original single potential is restored by stirring the surface. This very slow change of potential of the amalgam is in marked contrast to that of pure copper, where the true single potential is not constant for more than half a second.

The Standard Potential of Copper.—The absolute values obtained in the previous work were not very reliable for two reasons. (1) No thermostat was used owing to mechanical difficulties involved and the room temperature varied ±1° from 20° during the experiments and (2) the mercurous sulfate electrode was not fresh and showed signs of variation. The main conclusion from this work namely, that the single potentials of pure copper and two-phase copper amalgam are identical, is not affected by the above errors; we are therefore justified in using the convenient amalgam for the determination of the standard potential of copper against a normal solution of cupric ions.

This has already been done by Nielsen and Brown with considerable care but one point in their work is open to criticism. They preserved their amalgam under an acid solution of copper sulfate and the presence of this acid may possibly give rise to the appearance of traces of hydrogen in the electrode—a very dangerous impurity. They are well aware of the fact that freshly prepared copper shows abnormally high reducing power but took no precautions to ensure the absence of hydrogen in their amalgam. Their experiments were therefore repeated in the single case of the cell $Cu{\cdot}Hg \mid CuSO_4 \mid 0.5\ M\ Hg_2SO_4 \mid Hg$, using a thermostat adjusted to 25 ± 0.02°. All of the materials used were prepared by methods similar to those used by Nielsen and Brown except that the amalgam before use was heated to near the boiling point of mercury. The value obtained for the above cell in this work was 0.3596 volt, whereas Nielsen and Brown obtained 0.3592 volt. The difference between the two results is so small that it is evident that the amalgam prepared by Nielsen and Brown was free from hydrogen and their results may therefore be accepted as standard values for the pure copper electrode with a considerable degree of confidence.

How far their calculations for the potential of the normal copper electrode are justified is open to doubt since the activity equations break down at such high concentrations. If their value of 0.3502 volt referred to the hydrogen electrode be accepted, then taking the absolute potential of the normal hydrogen electrode as 0.285 volt, the absolute potential of the normal copper electrode will be 0.635 volt as compared with the values 0.60 to 0.62 volt previously given in the literature.

In view of the success of the above work it should be possible to determine the absolute potentials of iron, nickel and cobalt electrodes in the same way. Discrepancies in the values assigned to these metals are far greater than in the case of copper. Work along these lines is already in progress.

Part of the preliminary work was carried out in 1926 at this University by Mr. R. C. MacGaffin, to whom the author tenders his thanks.

Summary

The variations in the single potential of a copper electrode have been traced to the formation of insoluble films of basic cuprous or cupric salts on the electrode surface. These films are produced by the chemical action of the electrolyte upon the metallic copper, more rapidly in the presence of air, and may attain a thickness of 1 millimeter in a few days.

A method is described whereby the single potential of the copper electrode is measured before the film has time to form.

The single potential of a two-phase copper amalgam is identical with that of pure copper but much easier to measure with accuracy. Reasons for this are given.

Nielsen and Brown's work on the two-phase copper amalgam may be accepted as standard for pure copper.

The absolute potential of the normal copper (cupric) electrode is 0.635 volt if that of the normal hydrogen electrode is 0.285 volt.

CAPE TOWN, SOUTH AFRICA

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

FERROUS NITROSO COMPOUNDS

BY H. I. SCHLESINGER AND H. B. VAN VALKENBURGH[1,2]

RECEIVED SEPTEMBER 1, 1928 PUBLISHED MAY 6, 1929

When nitric oxide is passed into solutions of ferrous sulfate, the compound $FeSO_4 \cdot NO$ is formed. The work of Manchot,[3] of Kohlschütter,[4] and more recently of Schlesinger and Salathe,[5] has shown that there are two substances, one brown and one red, which have this composition. Schlesinger and Salathe have demonstrated that the brown compound exists in solutions containing up to about 55% acid, and that the red compound exists in solutions of acid concentration greater than 65%.[6] Between these limits the two compounds are apparently in equilibrium with each other.

Manchot has proved that the aqueous or dilute sulfuric acid solutions contain a complex ion of nitric oxide and ferrous iron by demonstrating that this ion travels to the cathode. About the compound existing in concentrated acid solutions, several views have been expressed. Manchot believes that the nitric oxide in the compound is attached to the ferrous sulfate molecule as a whole. Raschig[7] holds that it is a derivative of the hypothetical nitrosi-sulfonic acid, H_2SNO_5, and makes use of this hypothesis in demonstrating his theory of the lead chamber process. Kohlschütter, finally, is of the opinion that the effect of the sulfuric acid is due in part to auto-complex formation and in part to the dehydrating action of the acid. The latter view receives decisive support from the investigation herein reported.

Kohlschütter has already shown that ferrous chloride in alcoholic solutions reacts with nitric oxide, and that the compound formed in the presence of water is brown, like the ferrous sulfate complex, while in the alcoholic solutions a green color is obtained, and that the two have dif-

---

[1] This material is taken from a thesis to be presented by H. B. Van Valkenburgh to the Ogden Graduate School of Science in partial fulfilment of the requirements of the degree of Doctor of Philosophy. The work was completed in the summer of 1926.

[2] The work herein reported is part of a more comprehensive line of investigation undertaken with the assistance of a grant from the Bache fund of the National Academy of Sciences.

[3] Manchot, *Ann.*. 350, 368 (1906); 372, 153 (1910); Ber., 47, 1601 (1914); Z. *anorg. allgem. Chem.*, **140**, 22 (1924).

[4] Kohlschütter, Ber., 37, 3044 (1904); 40, 873 (1907); 44, 1423 (1911).

[5] Schlesinger and Salathe, THIS JOURNAL, 45, 1871 (1923).

[6] Manchot and Linckh, *Ber.*, 59, 406 (1926), apparently without knowledge of the earlier work of Schlesinger and Salathe, published data concerning the absorption spectra of various metal–nitroso compounds in different solvents and obtained results in close agreement with those found in this Laboratory. The question of the range of concentration in which the transition occurs was not studied by them.

[7] Raschig, *Z. angew. Chem.*, 18, 1281 (1905); *J. Soc. Chem. Ind.*, 30, 166 (1911).

ferent absorption spectra. The spectra obtained visually by Kohlschiitter are not accurate enough to be of use in deciding definitely whether they are of the same character as those of solutions of the ferrous sulfate–nitric oxide complex, or to determine at what concentration the transition from one compound to the other occurs. Photographs taken by us answer these questions more satisfactorily.

In Fig. 1 are shown the absorption spectra of the compound FeCl$_2$·NO when dissolved in water, in water alcohol mixtures and in absolute alcohol. An absorption band extending approximately from oscillation frequencies 1920 to 2320 is shown in 30, 70 and 90% alcohol. In the aqueous solution the band is somewhat narrower, but its right-hand margin and the region of maximum transmission are the same as for the alcohol–water mixtures. The slight difference observed may be accounted for by the fact that in solutions containing water the concentration of the complex is lower than in alcoholic solutions because its stability decreases as the concentration of alcohol decreases. Consequently at a given nitric oxide pressure (atmospheric in our experiments) less of the ferrous chloride is converted into the complex than in the solutions containing more alcohol. This fact also explains the greater depth of the band in alcoholic solutions. When absolute alcohol is used the band is definitely different from all of the others, showing with respect to them a displacement toward the red of both margins and of the region of maximum transmission.

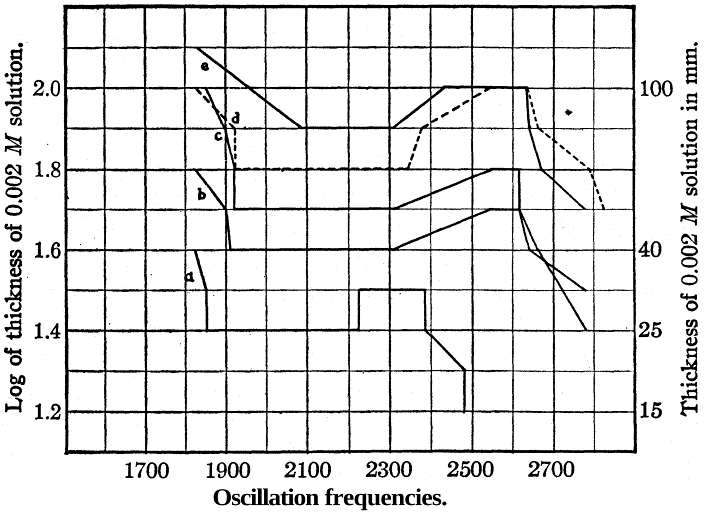


Fig. 1.--0.002 M FeCl$_2$·NO in alcohol of following concentrations: a = absolute, b = 90%, c = 70%, d = 30%, e = water solution.

Comparison of these spectra with those obtained by Schlesinger and Salathe[6] reveals several significant facts. As shown in Fig. 2, the spectra of the dilute alcoholic solutions of the complex $FeCl_2 \cdot NO$ are practically identical, so far as location of the band is concerned, with those of the less strongly acid solutions of the compound $FeSO_4 \cdot NO$. The slight differences which exist are unquestionably due in part to the difficulty of obtaining exact measurements of solutions so subject to contamination with actinic substances as are those under investigation, and in part to difference in the stability of the two solutions. The second point to be considered is

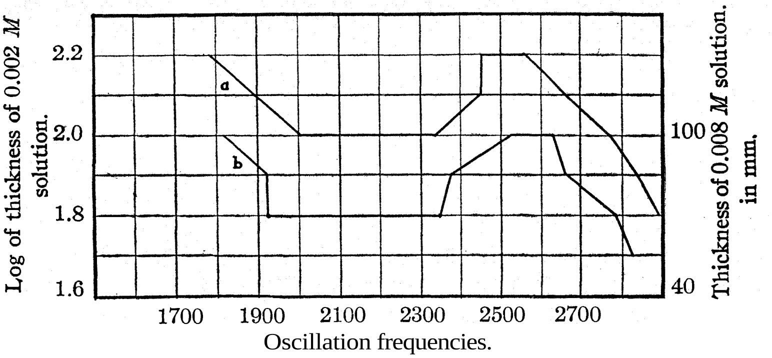


Fig. 2.—a = 0.0125 M $FeSO_4 \cdot NO$ in 45% H_2SO_4, after Schlesinger and Salathe; b = 0.002 *M* $FeCl_2 \cdot NO$ in 30% C_2H_5OH.

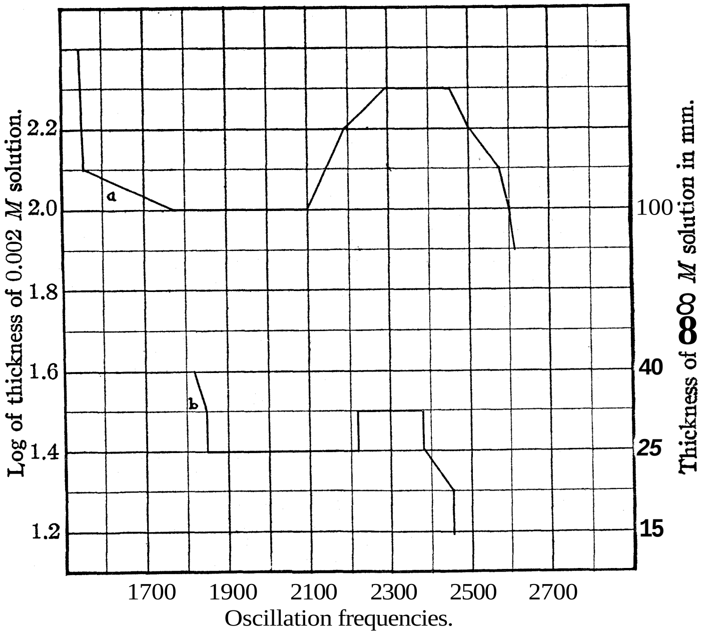


Fig. 3.—a = 0.0125 M $FeSO_4 \cdot NO$ in 93.1% H_2SO_4, after Schlesinger and Salathe; b = 0.002 M $FeCl_2 \cdot NO$ in absolute alcohol.

that both in the alcoholic solutions of $FeCl_2 \cdot NO$ and in the acid solution of $FeSO_4 \cdot NO$, decrease in the amount of water causes a similar shift in the absorption spectrum. It is true that the band in the concentrated sulfuric acid is not identical with that in absolute alcohol (See Fig. 3), a fact which will be discussed more fully below; but the spectra and their changes are sufficiently similar to point to the conclusion that the sulfate ion is not concerned in the reaction. They seem therefore to contradict the view of Raschig[7] that a salt of nitrosi-sulfonic acid is involved.

On account of the slight but definite differences between the spectra of $FeCl_2 \cdot NO$ in absolute alcohol and of $FeSO_4 \cdot NO$ in concentrated sulfuric acid, the results just described do not settle the problem definitely; hence we undertook a study of the behavior of the compound $FeHPO_4 \cdot NO$, the preparation of which has been described by Manchot.[8] In aqueous solutions it has the brown color characteristic of aqueous and slightly acid solutions of $FeSO_4 \cdot NO$. If phosphoric acid is added, the color changes and finally becomes cherry-red as the phosphoric acid becomes very concentrated. To show that this phenomenon is analogous to that with the sulfate, it is necessary to demonstrate that the change in color is not accompanied by a change in the ratio of ferrous salt to nitric oxide. For this purpose the procedure of Manchot was used; that is, as shown in Table I, the amount of nitric oxide absorbed per gram molecule of ferrous phosphate was determined, due allowance being made for the solubility of the gas in the concentrated acid used as solvent.

TABLE I

THE SOLUBILITY OR NITRIC OXIDE IN CONCENTRATED PHOSPHORIC ACID SOLUTIONS OF FERROUS PHOSPHATE

Acid, g.	Fe, g.	Concn. of Fe, mole	Temp.. °C.	Press.. mm.	NO absorbed by soln., cc.	NO absorbed at S. T. P. by $FeHPO_4$ per g. atom of Fe	
						Cc.	Liters
25.880	0.0034	0.004	26	625	7.4	1.18	19.6
20.880	.0027	,004	24	632	6.0	1.05	21.7
22.245	.0029	.004	25	626	6.6	1.20	23.1
23.521	.0030	.004	23	628	6.6	1.06	19.7
23.438	.0061	.008	23	628	8.8	2.75	25.2
21.549	.0056	.008	20	630	7.8	2.38	23.6
22.667	.0059	.008	20	632	8.4	2.67	25.3
25.820	.0067	.008	20	632	9.0	2.50	20.8
22.703	,0118	.016	20	626	10.8	4.44	21.0
						Av.	22.2

The data in the sixth column of the table represent the total volume of nitric oxide absorbed by the solution at the temperature and pressure indicated. The data in Col. 7 give the volume of nitric oxide, referred to standard conditions, absorbed by the ferrous phosphate alone; allowance

---

[8] Manchot, *Ber.*, 47, 1601 (1914).

is made for the solubility of the gas in the acid on the assumption that this solubility is the same in the solution as it is in the pure solvent. The solubility of nitric oxide in concentrated phosphoric acid, referred to standard conditions, was found to be 16.9 cc. per 100 g. of acid.

The fact that 22.2 liters of nitric oxide, referred to standard conditions, are absorbed, on the average, per gram atom of iron shows that the formula of the red compound, like that of the brown one, is $FeHPO_4{\cdot}NO$, except for the possibility of hydration, which will be discussed below. The variation in the data of Col. 8 is due to experimental error, as shown by the fact that it is entirely unrelated to changes in concentration of the solutions. The experimental difficulty is a secondary reaction of the nitric oxide with the ferrous salt, for if nitric oxide is passed through the solution for some time, the color entirely disappears as a result of oxidation of ferrous to ferric salt. It is, therefore, difficult to be sure that the solution is neither unsaturated nor treated with an excess of the gas.

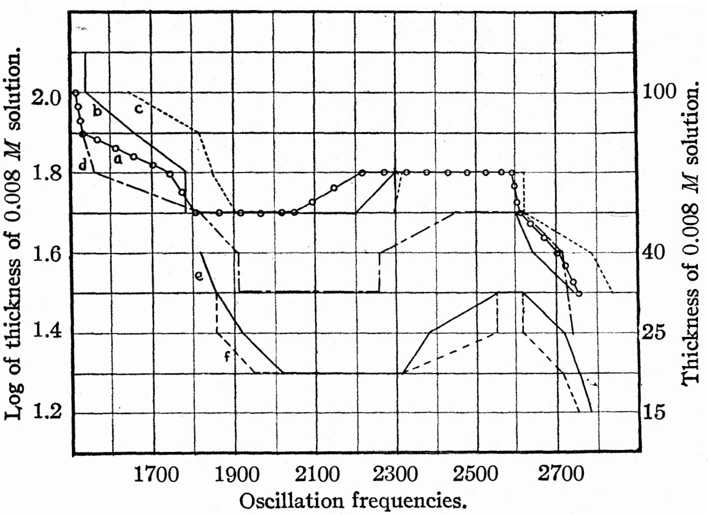


Fig. 4.—0.008 *M* $FeHPO_4{\cdot}NO$ in H_3PO_4 of following concentrations: a = 90%, b = 85%, c = 70%, d = 60%, e = 20%, f = 10%.

The absorption spectra of ferrous phosphate saturated with nitric oxide in solutions containing various amounts of phosphoric acid are shown in Fig. 4. The absorption band in solutions of 88 to 90% acid is almost identical in position with that of $FeSO_4{\cdot}NO$ in solutions of sulfuric acid stronger than 65%. As the phosphoric acid becomes more dilute the absorption band widens and shifts toward the violet end of the spectrum, as is the case when the concentration of sulfuric acid in solutions of $FeSO_4{\cdot}NO$ is decreased. In aqueous and dilute acid solutions the absorption spectra of the ferrous sulfate complex are again almost identical with those of the ferrous phosphate complex. For comparison Fig. 5 is reproduced from the work of Schlesinger and Salathe.

A study of the composition of the solvent in which the transition from one type of compound to the other occurs reveals a very significant relationship between the beginning and the completion of the shift of the absorption band and the aqueous tension of the solvent. The data for the latter could not all be found for the temperature at which our work was done. Consequently, the comparison for phosphoric and sulfuric acids is made at 0°, while the comparison of the sulfuric acid with the alcoholic solutions is made at 25°. There seems to be no reason to believe that the conclusions reached are, in any important way, affected by the discrepancy. In sulfuric acid the shift begins in 55% solution which has an aqueous tension at 0° of 1.04 mm., and is complete in 65% acid in which the aqueous tension is 0.36 mm. To have these same aqueous tensions phosphoric acid solutions must be, respectively, 68 and 88%, and it is exactly in this range that the transition occurs for the ferrous phosphate-nitric oxide complex. The solutions of sulfuric acid just mentioned have at 25° aqueous tensions of 6.5 mm. and 2.75 mm., respectively. These aqueous tensions are reproduced by 94 and 97% solutions of alcohol. Our observations show that the transition of the complex $FeCl_2 \cdot NO$ begins when the concentration of the alcohol is above 90% and is complete in absolute alcohol.[9]

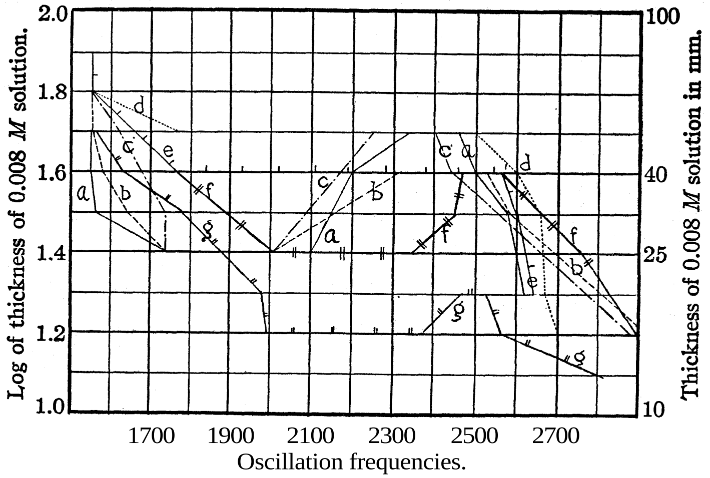


Fig. 5.—0.0125 M $FeSO_4 \cdot NO$ in H_2SO_4 of following concentrations: (taken from the work of Schlesinger and Salathe) a = 93.1%, b = 82.3%, c = 71.5%, d = 65.0%, e = 59.4%, f = 45.0%, g = 0%.

---

[9] The data for the aqueous tensions of the acid solutions are taken from Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., p. 1395, and those for the alcoholic solutions from Foote and Scholes, THIS JOURNAL, 33,1309 (1911).

The foregoing offers strong support for the conclusion that the transition in the three pairs of compounds having, respectively, the empirical formulas $FeSO_4 \cdot NO$, $FeHPO_4 \cdot NO$ and $FeCl_2 \cdot NO$, is in no way related to the nature of the negative ion but is determined by the activity of the water in the solution. The influence of the water is best explained by the assumption that in dilute aqueous solutions the positive ion in each case is $[Fe \cdot NO \cdot (H_2O)_x]^{++}$ and that the action of sulfuric acid, of phosphoric acid and of alcohol consists in removing all or part of the water in the complex ion. It is of interest to note that when Manchot attempted to prepare the solid brown compound $FeNOSO_4$ by precipitation with alcohol, he obtained a crystalline product containing ferrous sulfate and a much larger amount of water than that due to hydration of the ferrous sulfate present. Manchot also prepared the solid complex of nitric oxide and ferrous phosphate but the analytical data given by him refer only to the ratio NO:Fe and cannot be used to determine whether the salt is hydrated. On the other hand, Manchot and Linckh[10] found that the solid brown complex of ferrous selenate and nitric oxide, when precipitated from solutions containing water, alcohol and acetone, has the formula $FeSeO_4 \cdot NO \cdot 4H_2O$. These facts confirm the idea that in aqueous solutions hydrated complex ions are present; they cannot, however, be accepted as guides to judge of the formula of the complex.

That this is not the only factor involved in the alcoholic solutions of the ferrous chloride–nitric oxide complex is shown by the fact that the absorption spectrum of this substance in absolute alcohol is not quite identical with that of the solutions of complexes with the phosphate and the sulfate in the concentrated acids. According to Kohlschiitter the nitric oxide in alcoholic solutions of $FeCl_2$ is at least in part attached to a negative ion which also contains iron. He has therefore assumed that ferrous chloride is associated into $FeFeCl_4$ in these solutions, and that the nitric oxide reacts with the ion $FeCl_4$.[11] Our work does not bear on this phase of the problem. It does, however, emphasize the fact that dehydration of the aquo ion precedes formation of the chloro ion. This agrees with what is known to happen in the formation of the $CuCl_4$-ion from the hydrated cupric ion. The great similarity in the absorption spectra of $FeSO_4 \cdot NO$ in concentrated sulfuric acid and of $FeHPO_4 \cdot NO$ in concentrated phosphoric acid seems to indicate that the dehydrating action is the only function of the acids in these cases and that no complex ion containing iron, nitric oxide and the simple negative ion is formed. This

[10] Manchot and Linckh, *Z. anorg. allgem. Chem.*, **140,** 37 (1924).

[11] Our results explain why, in transference experiments, nitric oxide in alcoholic ferrous chloride solution is transported both to the anode and to the cathode. Since the transition from one type of compound to the other is not complete except in nearly 100% alcohol, the presence of water from the layer of diluted alcohol used causes a partial formation of the hydrated complex ion.

conclusion is supported by the fact that Kohlschiitter observed no transport of nitric oxide toward the anode in concentrated sulfuric acid solutions of $FeSO_4 \cdot NO$.[12]

An investigation was made to determine whether similar phenomena could be observed with other salts. Accordingly, the spectra of the following solutions were photographed before and after saturation with nitric oxide: nickel, cobalt and cadmium sulfates in water and sulfuric acid; cadmium chloride in water and in hydrochloric acid; nickel and cobalt chlorides in absolute alcohol. Cadmium chloride was studied because of its great tendency to form complexes, and cobalt and nickel sulfates because of the reports in the literature[13] that they dissolve appreciable quantities of nitric oxide. The spectrograms, however, failed to reveal even traces of complex ions in the solutions.

Experimental

It is not necessary to discuss in detail the experimental procedures because, in general, the methods and apparatus described by Schlesinger and Salathe were employed. The data obtained with the quartz spectrograph were in some instances supplemented by visual observations in the spectral region, for which the quartz instrument has small dispersion. Ferrous chloride was prepared by passing dry hydrogen chloride over hot iron wire in the absence of oxygen and was purified by sublimation. The product dissolves more slowly in concentrated than in dilute and very slowly in absolute alcohol, but no difficulty was encountered in finally obtaining solutions of the desired concentration. For the preparation of ferrous phosphate the method of Evans[14] was first tried but the analysis showed that only 79% of the iron in the product was in the ferrous condition, and the method was abandoned in favor of that of Debray.[15] Phosphoric acid of the desired concentration was obtained either by diluting the 85% acid with water or by heating it for several hours at 110–115° to obtain the stronger solutions. Weighed amounts of pure iron wire were then dissolved in the acid while a stream of oxygen-free hydrogen was passing through the solution. Thus were obtained solutions of ferrous salt free from ferric compounds and of the desired concentration. The solutions were then forced into the Baly tubes by a stream of hydrogen. The precautions mentioned by Schlesinger and Salathe for preventing access of oxygen to the tubes during the observations were taken.

Summary

Absorption spectra of the complexes formed by ferrous phosphate with nitric oxide in solutions of phosphoric acid of various concentrations, and by ferrous chloride with nitric oxide in alcohol solutions of various concentrations, have been photographed and found to be almost identical with those of the ferrous sulfate–nitric oxide complex in sulfuric acid.

---

[12] Too great stress, however, must not be placed on the transference experiments in concentrated sulfuric acid. In these solutions the conductance of the solvent is so high that only a small fraction of the current is carried by the solute, which is present in relatively small amounts.

[13] Hiifner, *Z. physik.* Chem., 59,416 (1907); Usher, *ibid.*, **62,022** (1908).

[14] Evans, ***Pharm.* J.**, [4] 4,141 (1897).

[15] Debray, *Ann. chim.*, **[3]** 61,437 (1861).

The shift of the absorption band toward the violet end of the spectrum, which occurs with increasing dilution of sulfuric acid solutions of ferrous sulfate saturated with nitric oxide, also occurs on diluting phosphoric acid solutions of ferrous phosphate, and alcohol solutions of ferrous chloride saturated with nitric oxide. This shift of the absorption band indicates a transition of one compound into another. The transition of the three pairs of compounds having, respectively, the empirical formulas $FeSO_4 \cdot NO$, $FeHPO_4 \cdot NO$, $FeCl_2 \cdot NO$ is probably determined in each case by the activity of the water in the solutions, that is, the transition occurs when the aqueous tensions of the solutions reach the same numerical value. This condition obtains when the concentrations of the three solvents H_2SO_4, H_3PO_4 and C_2H_5OH are, respectively, about 65, 88 and 97%.

The function of the concentrated acids and alcohol is probably largely that of dehydrating the complex ion which exists in dilute solutions.

CHICAGO, ILLINOIS

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

TEMPERATURE–CONDUCTANCE CURVES OF SOLID SALTS. II. HALIDES OF POTASSIUM AND THALLIUM

BY T. E. PHIPPS AND E. G. PARTRIDGE[1]

RECEIVED SEPTEMBER 6, 1928 PUBLISHED MAY 6, 1929

In a recent investigation[2] of temperature–conductance curves of the solid halides of sodium, the data in most cases showed two distinct slopes when plotted to the axes log k (logarithm of specific conductance) against $1/T$ (reciprocal of the absolute temperature). In the discussion of these data it was assumed that the conductance of the solid is proportional only to the number of ions in its lattice which have an energy greater than a certain threshold value and, further, that the mobility of these ions is nearly independent of the temperature. With these assumptions it was shown that the slope of the log k–$1/T$ curve may measure the threshold energy (designated as heat of liberation) which the conducting ion or ions must acquire in order to participate in the conduction process. To explain the existence at higher temperatures of a second slope, which was within experimental error double the slope at lower temperatures it was assumed[3] that at higher temperatures both ions take part in the conduction

---

[1] This paper is an abstract of a thesis submitted by E. G. Partridge in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Phipps, Lansing and Cooke, THIS JOURNAL, 48, 112 (1926).

[3] A subsequent investigation by Phipps and Leslie [*ibid.*, 50, 2412 (1928)] of transference numbers in solid sodium chloride at high temperatures gives definite evidence that both ions conduct at high temperatures.

process. At low temperatures experimental evidence has already been adduced in the case of sodium chloride that only the sodium ion conducts.[4]

In continuing this work it seemed desirable first to test the adequacy of the log k–$1/T$ relation to represent experimental data for uni-univalent salts of widely different polarity, and thus to determine whether or not the concept of heat of liberation of the conducting ion is a fundamental one. Second, if heat of liberation appears to be a fundamental lattice property, it is of interest to discover its possible relation to other lattice quantities such as the natural quantum of the lattice, the lattice energy and the property vaguely designated as polarity.

We may state briefly the principal results of this investigation. The log $k-1/T$ relation is judged to be adequate to represent the conductance data of both potassium and thallous halides. The two-slope behavior found previously for sodium halides also characterizes the conductance curves of potassium halides. Thallous halides show a single slope only. The heat of liberation of the potassium ion decreases in the series chloride to iodide, as in the sodium series. The heat of liberation of the potassium ion is distinctly greater than that for the sodium ion in the corresponding halide. An approximately linear relation exists in the sodium and potassium series between heat of liberation and melting point.

Experimental

Apparatus.—The conductivity apparatus was similar to that used previously except that the base was made from a large nickel disk about 6.5 cm. in diameter and 3.0 cm. in thickness, recessed to a depth of 1.5 cm. The diameter of the recessed hole was about 3.6 cm. This large mass of nickel served to smooth out temperature fluctuations of the furnace more effectively than had been the case with the old apparatus. An alternating current Wheatstone bridge method was used for resistances up to one megohm. For greater resistances the d. c. bridge method employed in the previous investigation was unsatisfactory due to the large polarization which it produced in the crystals. Accordingly a d. c. deflection method was adopted in which a variable e.m.f. and a high sensitivity galvanometer (figure of merit 7.76×10^{-10}, resistance 500 ohms, critical damping resistance 10,800 ohms) and a reversing switch were put in series with the crystal, the e.m.f. being so regulated that the amount of current flowing in the circuit was of the order of 10^{-8} amps. For resistances between 10^5 megohms and 50 megohms, voltages from 100 to 2 volts were obtained from radio "B" batteries, and for resistances between 50 and 10 megohms the variable e.m.f. in the circuit was replaced by a potentiometer source. At resistances greater than 30 megohms, reversal of the current through the crystal usually gave equal deflections in opposite directions. Between 30 and 10 megohms the deflections were often unsymmetrical and erratic, so that the d. c. points in this range are not considered reliable. This erratic behavior is due largely to polarization, and perhaps in part to the fact that unavoidable thermal e.m.f.'s became appreciable in this range in comparison with the applied e.m.f.

A platinum–platinum-rhodium thermocouple and Weston Universal potentiometer were substituted for the two-junction chromel–alumel couple and extended Student Type potentiometer used in the previous investigation. The temperature could be

---

[4] V. Seelen, Z. *Physik*, 29, 125 (1924).

kept constant to about 0.1°. Calibration of the noble metal couple on three occasions during the investigation, at the steam point, sulfur point and melting points of potassium chloride and potassium sulfate, showed a maximum variation of 0.7° at the fixed points and an average variation of 0.3°.

Materials.—The thallous halides were prepared from an old stock of Kahlbaum's thallous acetate by precipitation with the appropriate halogen acid. The work was carried out in a dark room as the thallous halides are sensitive to light. The acids were distilled in an all-pyrex apparatus and the middle fraction was used for the precipitation. The precipitates were washed thoroughly with conductivity water, dried, fused and poured into a clean iron die. The plunger was quickly inserted into the die after the pouring, and given a light tap with a hammer to form the pellet. Very satisfactory homogeneous pellets resulted. These were kept in dark glass bottles.

The potassium salts were "reagent quality" or "C. P." stock, recrystallized in all cases twice or thrice from conductivity water.

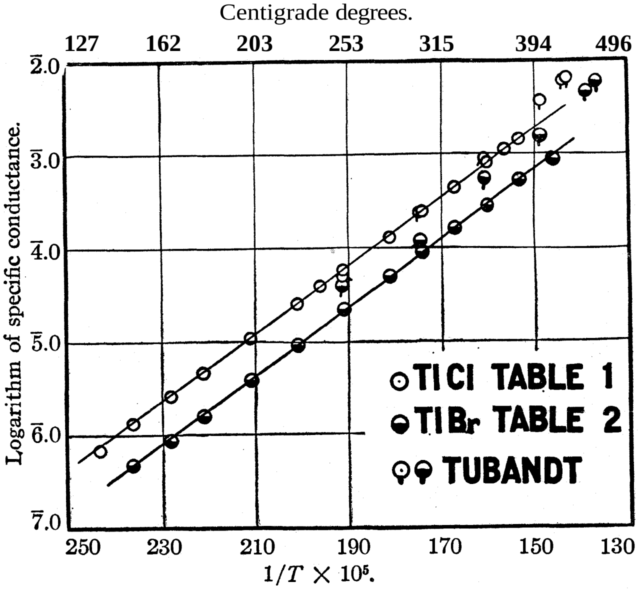


Fig. 1.—Conductance of thallous chloride and thallous bromide.

Preparation of Crystals and Pellets.—Crystals of potassium chloride and potassium bromide were grown by the method of Tammann and Veszi.[5] Visually perfect crystals from 0.5 to 1.0 cm. on edge, and 0.3 to 0.5 cm. thick were obtained. Attempts to grow crystals of potassium iodide were unsuccessful. Pellets of all the halides of potassium were made in a die with a specially hardened steel plunger at pressures of 230,000 lb. per sq. in. (16,200 kg. per sq. cm.). These pressures were somewhat higher than those applied in the case of sodium halides previously, since it was hoped that higher pressures would produce bodies which in their conduction process would approach more nearly to single crystal lattices. All three[6] halides gave translucent pellets. The bromide was more nearly transparent than the others.

---

[5] Tammann and Veszi, Z. *anorg. allgem. Chem.*, *150,* 355 (1926).

[6] On account of the hygroscopic character of potassium fluoride it could not be handled satisfactorily in the present apparatus and no data for it appear here.

Experimental Results

Thallous Halides.—In Figs. 1 and 2 are plotted the data for one run on each of the halides of thallium. These curves indicate the adequacy of the log *k*–1/*T* relation to represent the experimental data in these cases. For all the thallous halides the conductivity readings were very distinct and reproducible. This high degree of reproducibility is a matter of interest. It seems to indicate that polarization may depend upon lattice rigidity and may vary in degree on passing from the brittle polar salts, where restoring forces are strong, to the waxy salts where these forces are relatively weak. The change in crystal form in thallous iodide is strikingly shown in Fig. 2.

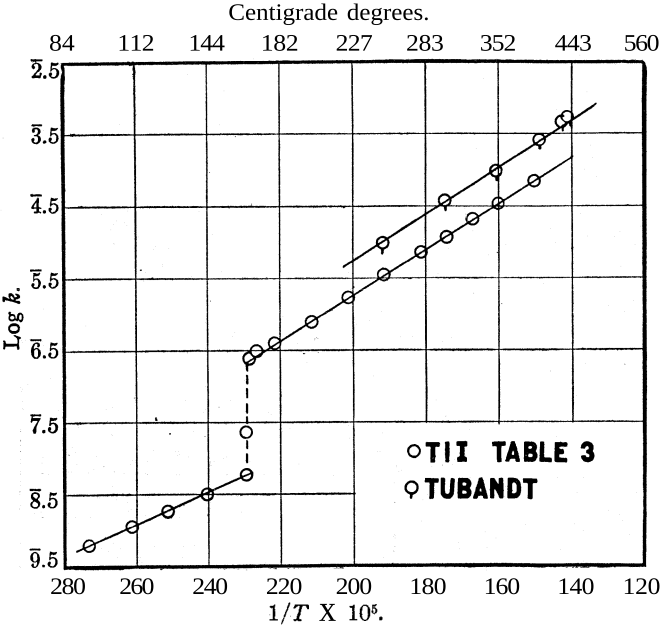


Fig. 2.—Conductance of thallous iodide.

Table I

Thallous Chloride

1/*T* × 10^5	153	156	160	167	174	181	191
Log k	$\bar{3}.152$	$\bar{3}.045$	3.910	$\bar{4}.643$	$\bar{4}.391$	$\bar{4}.110$	$\bar{5}.762$
1/*T* X 10^5	196	201	211	221	228	236	243
Log *k*	$\bar{5}.585$	$\bar{5}.405$	$\bar{5}.033$	$\bar{6}.662$	$\bar{6}.408$	$\bar{6}.120$	$\bar{7}.833$

The heat of liberation calculated from the above data was 11.57 × 10^{-13} ergs per ion. Two other independent runs under identical conditions gave the values 11.50 and 11.38 X 10^{-13}. The average for the three runs was 11.48 X 10^{-13}.

TABLE II

THALLOUS BROMIDE

$1/T \times 10^5$	146	153	160	167	174	181
Log k	$\bar{4}.942$	$\bar{4}.718$	$\bar{4}.450$	$\bar{4}.207$	$\bar{5}.958$	$\bar{5}.701$
$1/T \times 10^5$	191	201	211	221	228	236
Log k	$\bar{5}.344$	$\bar{6}.956$	$\bar{6}.581$	$\bar{6}.201$	$\bar{7}.928$	$\bar{7}.668$

The heat of liberation from the above data was 11.68 X 10^{-13} ergs *per* ion. Another independent run gave 11.60 X 10^{-13}. The average was 11.64 × 10^{-13}.

TABLE III

THALLOUS IODIDE

$1/T \times 10^5$	150	160	167	174	181	191	201	211	221
Log k	$\bar{4}.863$	$\bar{4}.541$	$\bar{4}.326$	$\bar{4}.086$	$\bar{5}.869$	$\bar{5}.549$	$\bar{5}.243$	$\bar{6}.905$	$\bar{6}.605$
$1/T \times 10^5$	226	228	229	229	240	251	261	273	
Log k	$\bar{6}.500$	6.396	7.375	8.777	$\bar{8}.512$	$\bar{8}.279$	8.068	$\bar{9}.810$	
			(a.c.)	(d.c.)					

The heat of liberation from the above data for the upper slope was 10.2 X 10^{-13} ergs per ion and for the lower slope 6.6 X 10^{-13}. Two other runs under identical conditions gave for the upper slope 10.2 and 9.7 × 10^{-13}. The average of three runs gave for the upper slope 10.0 X 10^{-13}.

Potassium Halides. A. C. Values in the Transition Range.—In Fig. 3 it will be noted that the a. c. points veer off at a temperature of about 550° from the straight line upon which the high temperature points lie, and that the a. c. curve becomes almost horizontal at about 350". Tammann and Veszi's points for potassium chloride crystal show a similar behavior. However, these investigators did not follow the curve lower than a temperature of 520°, and it is below this temperature that the anomalous behavior of the a. c. conductance values becomes most striking. A similar example of the a. c. anomaly may be seen in Fig. 5, in the case of potassium bromide crystals. A complete explanation of this behavior is lacking. It was thought at first that large high-frequency currents might be carried by a capacity effect in the crystal. However, calculation showed that the fraction of the total current which could be carried by the capacity effect (even with an assumed dielectric for the salt as great as 20) is negligibly small when 1000-cycle current is used as in the present case. The suggestion has been made that these abnormally high a. c. conductances may be explained as due to a carrying of high-frequency overtones of the alternating current by oscillation of the ions of the lattice. As lending slight experimental support to this suggestion, it may be seen that the a. c. anomaly in the transition range is less marked in the case of conglomerates (pellets) (see Figs. 4, 6 and 7) than in the case of crystals (Figs. 3 and 5). Oscillation currents would be expected to be greater in the more perfect lattice of the crystal than in the conglomerate. It is significant that the anomalous a. c. values occur in the temperature interval where we have evidence from transference numbers that the conduction process is changing from uni-ionic to bi-ionic conduction. It is possible that the impressed a. c. affects the transition from one type of conduction to the other. The conclusion of Tammann and Veszi that the log k–T relation represents the course of the conductance curve in the high temperature range better than the log k–1/T relation will perhaps need to be modified if due account is taken of the a. c. anomaly.

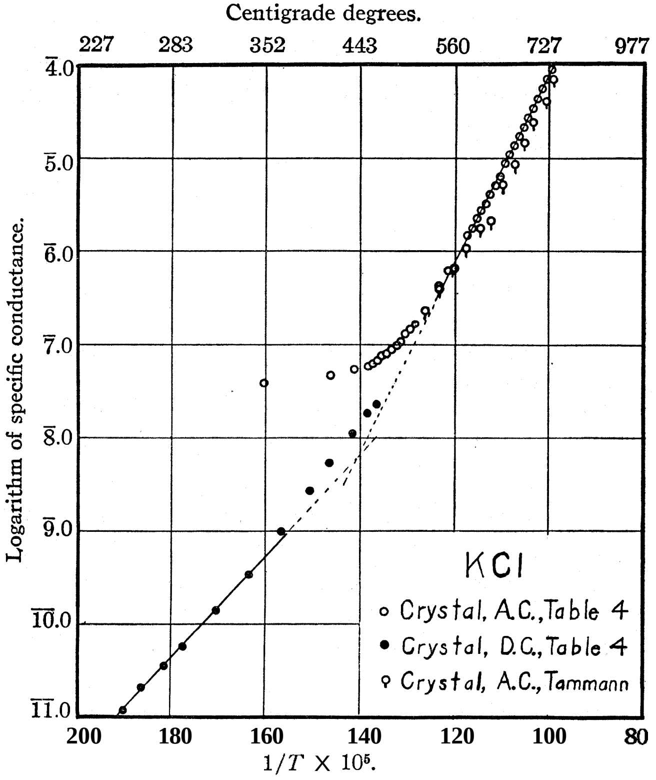


Fig. 3.—Showing (1) anomalous a. c. behavior; (2) the one-half relation between the lower and upper slopes; (3) Tammann and Veszi's crystal data.

TABLE: IV

POTASSIUM CHLORIDE CRYSTAL

1/T × 10'	Log k	1/T × 10⁵	Log k	1/T × 10⁵	Log k
98	3.057	114	$\bar{6}.452$	138	8.783
99	$\bar{5}.959$	115	$\bar{6}.357$	141	$\bar{8}.752$
100	$\bar{5}.858$	116	6.264	146	8.685
101	5.755	117	$\bar{6}.181$	160	8.607
102	$\bar{5}.650$	121	5.797	191	$\overline{11}.082$
103	$\bar{5}.543$	123	$\bar{7}.632$	186	11.328

TABLE IV (Concluded)

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
104	$\bar{5}.444$	126	$\bar{7}.368$	181	$\overline{11}.570$
105	$\bar{5}.351$	128	$\bar{7}.242$	177	$\overline{11}.771$
106	$\bar{5}.250$	129	$\bar{7}.179$	170	$\overline{10}.148$
107	$\bar{5}.151$	130	$\bar{7}.125$	163	$\overline{10}.536$
108	$\bar{5}.053$	131	$\bar{7}.041$	156	$\overline{10}.968$
109	$\bar{6}.955$	132	$\bar{7}.002$	150	9.442
110	$\bar{6}.818$	133	$\bar{8}.958$	146	$\bar{9}.744$
111	$\bar{6}.724$	134	$\bar{8}.923$	141	$\bar{8}.056$
110	$\bar{6}.816$	135	8.889	138	$\bar{8}.271$
112	$\bar{6}.623$	136	$\bar{8}.843$	136	$\bar{8}.368$
113	$\bar{6}.523$	137	$\bar{8}.812$		

The heat of liberation from the above data for the upper slope was 31.9 × 10^{-13} ergs per ion, and for the lower slope 16.0 X 10^{-13}. Five other runs under identical conditions gave for the upper slope 31.7, 33.0, 32.2, 32.9 and 31.1 × 10^{-13}, and for the lower slope 15.1 and 16.0 × 10^{-13}. The average of six values for the upper slope was 32.1 × 10^{-13}, and the average of three values for the lower slope was 15.7 × 10^{-13}.

TABLE V

POTASSIUM CHLORIDE PELLET

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
98	$\bar{4}.074$	131	$\bar{7}.746$	186	$\bar{9}.131$
100	$\bar{5}.861$	136	$\bar{7}.536$	181	$\bar{9}.348$
103	$\bar{5}.550$	141	$\bar{7}.346$	177	$\bar{9}.523$
106	$\bar{5}.270$	146	$\bar{7}.168$	172	$\bar{9}.751$
108	$\bar{5}.097$	206	$\overline{10}.218$	167	$\bar{9}.973$
111	$\bar{6}.860$	201	$\overline{10}.441$	162	$\bar{8}.191$
116	6.524	196	$\overline{10}.679$	156	$\bar{8}.446$
121	6.226	191	$\overline{10}.901$	150	8.699
126	$\bar{7}.971$				

The heat of liberation from the above data for the upper slope was 30.5 and for the lower slope 14.2 × 10^{-13} ergs per ion. Three other runs under identical conditions gave for the upper slope 30.0, 30.3 and 30.3 X 10^{-13}, and another run gave for the lower slope 15.2 X 10^{-13}. The average of four values for the upper slope was 30.3 × 10^{-13}, and the average of two runs for the lower slope was 14.7 × 10^{-13}.

D. C. Values in the Transition Range.[7]—It will be noted in Pig. 3 that at the lowest temperatures (250–350°) the d. c. points lie upon a straight line, but between 350 and 450° they diverge considerably in the direction of conductance greater than the expected. In this transition region of temperature, namely, 350 to 500° for potassium chloride and 300–450° for potassium bromide (Fig. 5), there is probably a profound change in the conduction process. The polarization e.m.f. is no longer negligible com-

[7] Since this account was written the treatment by Joffe [Joffe, "The Physics of Crystals," McGraw-Hill Book Co., New York, 1928, p. 75 ff.] of the polarization e.m.f. in crystals has come to the attention of the writer. Adequate data are not at hand for correcting our transition range values according to his methods. Below the transition range the polarization is undoubtedly negligible compared with the applied potential.

pared with the applied e.m.f., and the course of the curve is very uncertain throughout this range.

TABLE VI

POTASSIUM BROMIDE CRYSTAL

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
196	$\overline{12}.476$	153	$\bar{9}.138$	111	$\bar{6}.975$
193	12.717	150	$\bar{9}.406$	112	6.890
190	$\overline{12}.848$	146	$\bar{9}.742$	113	$\bar{6}.794$
187	$\overline{12}.988$	143	$\bar{9}.995$	114	$\bar{6}.704$
184	$\overline{11}.118$	141	$\bar{9}.290$	115	8.605
181	$\overline{11}.273$	138	$\bar{8}.332$	116	$\bar{6}.514$
178	$\overline{11}.414$	102	$\bar{5}.900$	117	$\bar{6}.421$
175	$\overline{11}.577$	103	$\bar{5}.791$	118	$\bar{6}.340$
172	$\overline{11}.726$	104	$\bar{5}.687$	121	$\bar{6}.095$
169	$\overline{11}.922$	105	$\bar{5}.584$	126	$\bar{7}.772$
166	$\overline{10}.159$	106	$\bar{5}.480$	131	$\bar{7}.500$
163	$\overline{10}.460$	107	9.375	136	$\bar{7}.324$
160	$\overline{10}.754$	108	$\bar{5}.274$	141	7.220
160	$\overline{10}.621$	109	8.178	146	$\bar{7}.168$
156	$\overline{10}.908$	110	$\bar{5}.078$		

The heat of liberation from the above data for the upper slope was 31.4 X 10^{-13} and for the lower slope 15.0 X 10^{-13}. One other run under identical conditions gave for the upper slope 31.3 and for the lower slope 15.9 × 10^{-13}. The average of two runs gave for the upper slope the value 31.3 and for the lower slope 15.4 X 10^{-13}.

TABLE VII

POTASSIUM BROMIDE PELLET

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
243	$\overline{11}.129$	188	$\bar{9}.670$	110	9.259
238	$\overline{11}.382$	183	$\bar{9}.887$	111	$\bar{5}.180$
233	$\overline{11}.587$	178	$\bar{8}.093$	112	$\bar{5}.107$
228	$\overline{11}.822$	102	$\bar{4}.002$	113	$\bar{5}.036$
223	$\overline{10}.072$	103	$\bar{5}.809$	116	$\bar{6}.842$
218	$\overline{10}.305$	104	$\bar{5}.803$	121	$\bar{6}.598$
213	$\overline{10}.542$	105	$\bar{5}.708$	126	$\bar{6}.386$
208	$\overline{10}.774$	106	$\bar{5}.610$	131	$\bar{6}.204$
203	$\bar{9}.008$	107	$\bar{5}.518$	136	$\bar{6}.014$
197	$\bar{9}.278$	108	5.430	141	7.844
193	$\bar{9}.461$	109	$\bar{5}.344$	150	$\bar{7}.540$

The heat of liberation from the above data for the upper slope was 29.4 X 10^{-13} ergs per ion and for the lower slope 14.7 × 10^{-13}. Another run under identical conditions gave for the upper slope 29.0 and for the lower slope, 14.1 X 10^{-13}. The average of the two runs for the upper slope was 29.2 and for the lower slope 14.4 X 10^{-13}.

Differences between Conduction in Crystals and Pellets.—Figures 4 and 6 show the difference in conductance between pellets and crystals. The discrepancy is seen to be greater at lower temperatures, the pellet tending to have a slightly lesser slope. It will be noted in all of these cases that the uncertainty of the d. c. points in the transition range is less for the pellets than for the crystals. It seems to be generally true that polarization is less in the conglomerate than in the crystal. This is readily seen by comparing pellets of potassium chloride (Fig. 4) with crystals of potassium chloride (Fig. 3). In the case of the pellet the d. c. points fall regularly on a straight line to conductances greater than 10^{-8}, while in the case of the crystal there is a marked deviation even at conductances less than 10^{-9} reciprocal ohms. A second striking difference between the behavior of crystal and pellet is that the change in slope (and presumably the change in the conduction process also) occurs at a much higher temperature for the pellet than for the crystal. For example, in Fig. 3 for the crystal the intersection of the two slopes (produced) is at approximately 440°. On the other hand, in Fig. 4 for the pellet the corresponding intersection comes at a temperature of approximately 570°. Similarly for the potassium bromide crystal in Fig. 5 the intersection comes at

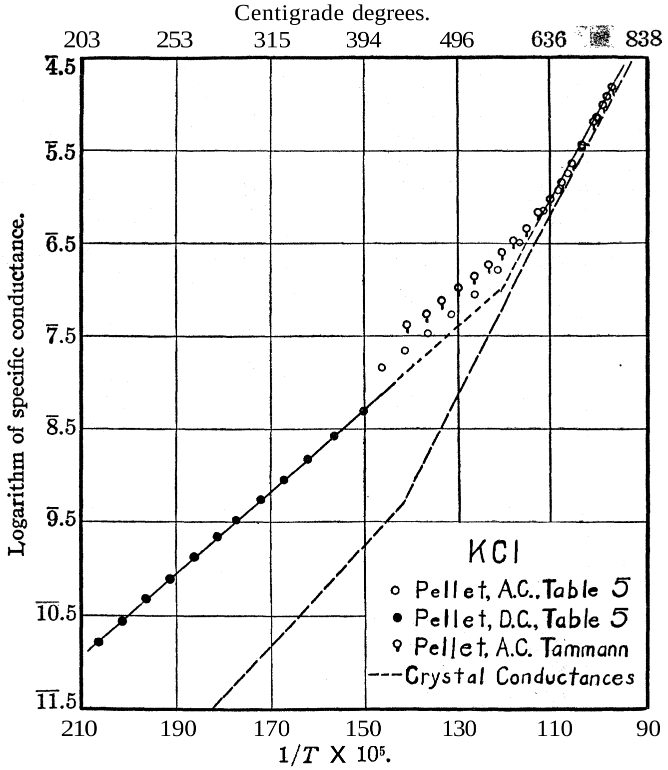


Fig. 4.—Showing (1) the higher conductance and lesser slope of pellets as compared with crystals at lower temperatures; (2) the merging of pellet and crystal data at higher temperatures; (3) Tammann and Veszi's pellet data.

approximately 370 and for the potassium bromide pellet in Fig. 6 it comes at about 600°. A third point of difference between pellet and crystal is that the heat of liberation is slightly less for the pellet than for the crystal. This is shown in Table IX. Potassium chloride crystals, for example, show values of 15.7 and 32.1 × 10^{-13} ergs/ion, calculated from the lower and upper slopes, respectively. The corresponding values for potassium chloride pellets are 14.7 and 30.3 × 10^{-13} ergs/ion.

TABLE VIII

POTASSIUM IODIDE PELLETS

$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k	$1/T \times 10^5$	Log k
Number 1		145	$\bar{7}.270$	109	$\bar{5}.818$
106	5.839	146	$\bar{7}.212$	110	$\bar{5}.733$
107	5.758	147	$\bar{7}.165$	111	$\bar{5}.648$
108	$\bar{5}.688$	148	$\bar{7}.128$	112	$\bar{5}.563$
109	$\bar{5}.608$	149	$\bar{7}.098$	113	5.492
110	$\bar{5}.529$	150	$\bar{7}.078$	114	$\bar{5}.414$
111	$\bar{5}.448$	156	$\bar{8}.962$	115	$\bar{5}.348$
112	$\bar{5}.374$	201	$\overline{10}.454$	116	$\bar{5}.277$
113	$\bar{5}.301$	196	$\overline{10}.638$	117	$\bar{5}.208$
114	$\bar{5}.230$	191	$\overline{10}.832$	128	$\bar{6}.487$
115	$\bar{5}.158$	186	$\bar{9}.042$	139	$\bar{7}.840$
116	$\bar{5}.088$	181	$\bar{9}.236$	201	$\overline{10}.891$
117	$\bar{5}.024$	177	$\bar{9}.379$	196	$\bar{9}.091$
118	$\bar{6}.959$	174	$\bar{9}.500$	191	$\bar{9}.298$
119	$\bar{6}.892$	170	$\bar{9}.676$	186	$\bar{9}.502$
123	6.631	167	$\bar{9}.804$	181	$\bar{9}.702$
126	$\bar{6}.440$	163	$\bar{9}.981$	177	$\bar{9}.853$
128	$\bar{6}.320$	160	8.176	172	$\bar{8}.074$
131	$\bar{6}.110$	156	8.332	167	8.277
133	$\bar{7}.981$			162	$\bar{8}.510$
136	$\bar{7}.800$	Number 2		156	8.776
139	$\bar{7}.634$	106	$\bar{4}.100$	150	8.998
143	$\bar{7}.358$	107	$\bar{5}.994$	146	$\bar{7}.483$
144	$\bar{7}.311$	108	$\bar{5}.903$		

The heat of liberation from the data of Pellet No. 1 for the upper slope was 24.0 and for the lower slope, 12.5 × 10^{-13} ergs per ion. For Pellet No. 2 the upper slope gave 25.6 and the lower slope 13.0 X 10^{-13}. Another run under identical conditions gave for the upper slope 27.5 and for the lower slope 15.0. The average of the three runs gave for the upper slope 25.7 and for the lower slope 13.5 × 10^{-13}.

Discussion of Results

The Conduction Process.—Two slopes were found for all the halides of sodium and potassium investigated, with the exception of sodium fluoride.[8] Single slopes only were found for thallous chloride and bromide.

---

[8] The anomalous behavior of sodium iodide and sodium fluoride in the neighborhood of the melting point, reported in the previous paper, is now thought to be due to impurities. Extremely pure sodium iodide and potassium iodide failed to show the sudden rise in conductance reported for sodium iodide.

Two slopes were found for thallous iodide, but in this case it is well known that the change in slope arises from a change in crystal form. In the case of all of the halides of sodium and potassium which exhibit two slopes, the upper slope is approximately double the lower slope. That the conduction at lower temperatures is due to the alkali metal ion only is shown by the transference experiment of v. Seelen[4] upon sodium chloride at 400°, and by the transference experiments of Phipps and Leslie[5] upon sodium chloride between 410 and 510°. Indirect evidence pointing to the same conclusion is seen in the work of Schmidt,[9] who found at lower temperatures that one ion only (usually the positive ion) was emitted from solid salts. At higher temperatures Schmidt found that both ions were emitted from solid salts in nearly all cases. In agreement with this, transference data now available[3] for sodium chloride between the temperatures of 558 and 655° indicate that both ions take part in the conduction process over this range of temperature.

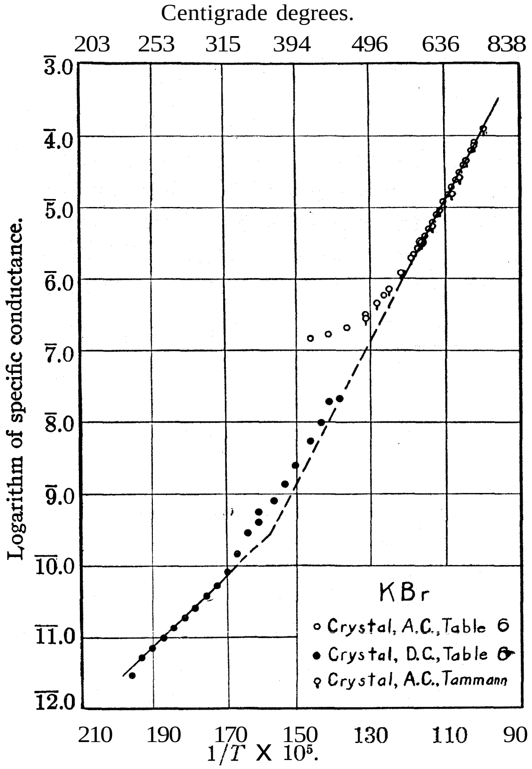


Fig. 5.—Showing (1)the one-half relation between lower and upper slopes; (2) deviation of both a. c. and d. c. points at intermediate temperatures; (3) Tammann and Veszi's crystal data.

Change from uni-ionic to bi-ionic conduction is exhibited by the chlorides, bromides and iodides of both sodium and potassium. This phenomenon appears to be characteristic of, and perhaps limited to, high-melting polar salts, since it is not shown by the halides of silver, thallium or lead.

The Adequacy of the Log *k*-1/*T* Relation.—The log k–1/T relation fits the data admirably in the case of the thallous halides over a range of temperature from 150° to temperatures within 30" of their melting points. In the case of the potassium halides we have already pointed out the need for caution in accepting the results of either an a.-c. or an uncorrected

---

[9] G. C. Schmidt, *Ann. Physik,* 80, 588 (1926).

TABLE IX

ILLUSTRATING DIFFERENCES BETWEEN HEATS OF LIBERATION IN CRYSTALS AND IN PELLETS

		$\epsilon \times 10^{13}$ ergs/ion	
Salt	Form	Lower slope	Upper slope
KCl	Crystal	15.7	32.1
	Pellet	14.7	30.3
KBr	Crystal	15.4	31.3
	Pellet	14.4	29.2
KI	Crystal	..	..
	Pellet	13.6	25.7

d.-c. method in the transition range where the conduction process is changing, and where polarization effects are greatest. If greater weight is given to the points in the two regions where reproducibility of measurement is the greatest, namely, to those a.-c. points which are well above

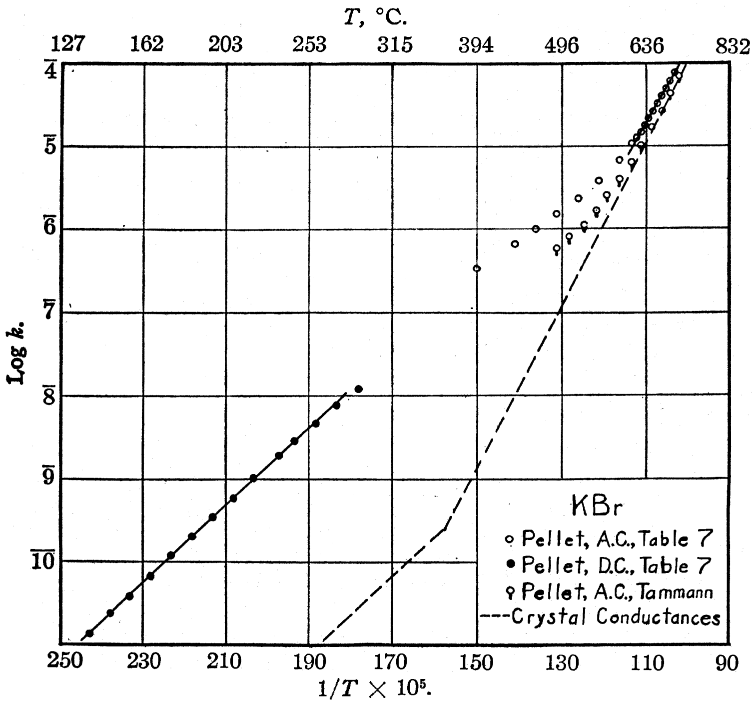


Fig. 6.—Showing (1) the one-half relation between lower and upper slopes; (2) higher conductance of pellet as compared with crystal; (3) Tammann and Veszi's pellet data.

the transition range, and to those d.-c. points which are well below it, the log k–$1/T$ relation is entirely adequate. The remarkable success of the log k-$1/T$ relation in the thallous series where polarization is a minimum and the conduction process uniform, gives us considerable confidence in its application to the less regular data of the polar salts where marked polarization accompanying the change in the conduction process has hitherto caused doubt in the choice between the log $k-1/T$ and the log k–T relation.

Heats of Liberation.—In Table X are summarized values for the heats of liberation of the halides of sodium, potassium and thallium. We may

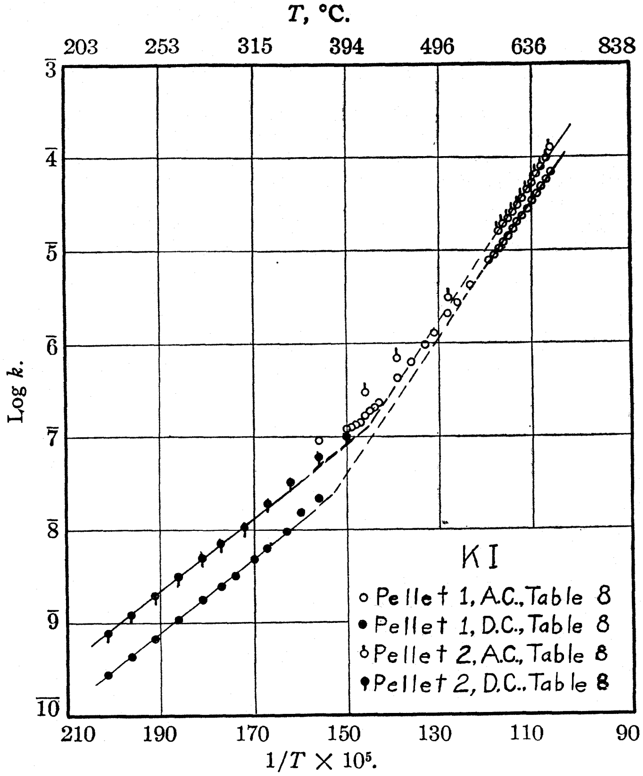


Fig. 7.—Showing (1) the one-half relation between the lower and upper slopes; (2) agreement in slope of two runs upon different pellets.

say provisionally that the values in Col. 3 are the heats of liberation of the positive ion, and the values in Col. 4 the heats of liberation of both positive **and** negative ions of the lattice in each case. On comparing Cols. 3 and 4 it is evident that in six cases the heat of liberation calculated from the upper slope is within experimental error double that from the lower slope. In the upper temperature range the lattice is "loosened," and whenever a positive ion of exceptional energy takes part in the conduction process it appears that a negative ion also receives the activating energy.

TABLE X

SUMMARY OF HEATS OF LIBERATION

Salt	M. p., °K.	AH, cal./g.-ion (lower slope)	AH, cal./g.-mole (upper slope)
NaCl	1077	20200	39800
NaBr	1028	18400	38400
NaI	924	13800	28300
KC1	1043"	22800	46600
KBr	1006"	22400	45400
KI	952"	19600	37200
T1C1	702"	16700	....
TlBr	732"	17000	....
TlI	713	14600	(9600)[b]

[a] Redetermined for the salts used in this investigation.

[b] Change in crystal form accounts for the existence of an upper slope in this case.

It will be noticed that the potassium ion has a larger heat of liberation than has the sodium ion in the same halide lattice, corresponding to the common conception of the potassium halides as more polar than the sodium halides. The heat of liberation in the thallous series is less than in the sodium or potassium series. Furthermore, the decrease in the heat of liberation (just as the decrease in melting point) is less in the sequence thallous chloride to iodide than the corresponding decreases in the other series. In the sodium and potassium series, heats of liberation (Col. 4) are approximately proportional to the absolute temperature of the melting point (Col. 2), within each series. In the thallous series the iodide, which changes crystal form, shows a departure from this rule.

In the study of the sodium series[2] it was shown that the ratio, heat of liberation per ion divided by the natural lattice quantum (as calculated from specific heat data), was roughly constant and had a value of about 40. A similar calculation from meager specific heat data for the potassium series gave values as follows: for potassium chloride, 51; for potassium bromide, 62; for potassium iodide, 60; average, 58. Further data are necessary before any conclusions can be drawn as to a possible relation between heat of liberation and natural quantum of the lattice.

The lattice energy of potassium chloride as calculated by Born is 163,000 cal. per gram-mole. The heat of liberation per gram-mole of potassium chloride (Col. 4, Table X) is about 47,000 cal.

Thus it appears that two oppositely charged ions which attain the threshold conduction energy in a potassium chloride lattice have less than one-third of the energy necessary to remove them completely from the lattice.

Summary

Temperature–conductance curves for the solid halides of potassium and thallium have been determined over wide temperature ranges. As in the case of the sodium halides two distinct slopes were observed for the potassium salts when the data were plotted to the axes log k (specific conductance) *versus* $1/T$. Only one slope was observed for thallous halides except in the case of thallous iodide, which undergoes a change of crystal form. In the light of recent high-temperature transference experiments, it is concluded that in the polar lattices only the positive ion conducts at lower temperatures, but that both ions conduct at higher temperatures. Change from uni-ionic to bi-ionic conduction seems to be characteristic of, and limited to, high-melting polar salts. Heats of liberation of the conducting ions in the various lattices have been calculated from the corresponding slopes. Within the sodium and potassium series heats of liberation are proportional to the melting points.

URBANA, ILLINOIS

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

A STUDY OF THE CALCIUM AMALGAM ELECTRODE IN DILUTE AQUEOUS SOLUTIONS[1]

BY RUSSEL JOHN FOSBINDER

RECEIVED SEPTEMBER 10, 1928 PUBLISHED MAY 6, 1929

The determination of the calcium-ion activities in dilute solutions of calcium salts by the measurement of the electromotive force of a cell of the proper type is interesting for two reasons. First, the electrochemical behavior of calcium amalgams against aqueous solutions of calcium salts apparently discloses many peculiarities not exhibited by other amalgam electrodes. Second, calcium-ion concentration is a matter of considerable importance in physiological chemistry.

Byers[2] attempted to determine equilibrium conditions in a system of calcium hydroxide and sodium carbonate by means of the electromotive-force method. Neuhausen and Marshall[3] studied the electrolyte equilibrium in the blood by the use of amalgam electrodes. Lucasse[4] measured the potentials of cells with and without liquid junctions to determine transference numbers and activity coefficients of the alkaline earth chlorides. Drucker and Luft[5] made a careful and critical study of the calcium electrode in solutions of calcium. Kirk and Schmidt[6] attempted to measure the calcium-ion activities in solutions of certain protein salts but stated that their technique was entirely inadequate.

---

[1] This communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1928 under the direction of Farrington Daniels.

[2] Byers, THIS JOURNAL, 30, 1584 (1908).

[3] Neuhausen and Marshall, *J. Biol. Chem.*, *53*, 365 (1922).

[4] Lucasse, THIS JOURNAL, 47, 743 (1925).

[5] Drucker and Luft, *Z. physik. Chem.*, 121, 307 (1926).

[6] Kirk and Schmidt, *J. Biol. Chem.*, *76*, 115 (1928).

The purpose of this investigation was to develop an apparatus and a technique suitable for the accurate determination of the effective calcium-ion concentration in dilute solutions, and also to study the possibility of applying the electrode in determining the state of calcium in solutions of physiological importance.

The Determination of Activity Coefficients of Calcium Chloride.—The activity coefficients of calcium chloride were determined from 0.01–**3.3** M in order to become familiar with the technique involved in the operation of the calcium electrode. The apparatus used and the method of procedure for the cells were, in general, similar to those described by Lucasse.[4] The calcium amalgam was prepared electrolytically according to the method prescribed by Neuhausen.[7] In making the determinations one cell was always filled with 0.0099 M calcium chloride, while the concentration of the solution in the other cell was varied at will. It was found that it was not necessary to have the solutions flowing, provided the readings were taken immediately after the amalgam flow was started. By such a procedure steady, reproducible potentials were obtained.

In Table I are given the results, where m is the number of moles of salt dissolved in 1000 **g.** of solvent, E is the electromotive force generated in the cell and γ is the activity coefficient.

TABLE I

DATA OBTAINED FOR CELLS OF THE TYPE Ag | AgCl | $CaCl_2$ (m) | Ca_xHg | $CaCl_2$ (m = 0.0099) | AgCl | Ag

m	E	γ	m	E	7
0.0099	0.00000	(0.716)	0.3069	0.11735	0.481
.0435	.04870	.572	.7158	.15605	.577
.0628	.06070	.550	1.2081	.18289	.689
.0781	,06885	.534	1.5378	.20232	.871
.0897	.06685	.494	1.9833	.21702	.974
.1411	.08940	.499	3.2702	27665	2.820

For a concentration cell without liquid junction containing a bi-univalent salt, the electromotive force, activity coefficient and concentration are related according to the equation

$$E = \frac{RT}{NF}\ln\left(\frac{\gamma_1\ 2^{2/3}m_1}{\gamma_2\ 2^{2/3}m_2}\right)^3 = \frac{3RT}{2F}\ln\frac{\gamma_1\ m_1}{\gamma_2\ m_2}$$

In calculating the values of the activity coefficient, it was assumed, as Lucasse assumed, that γ is 0.716 at 25° for the 0.0099 M $CaCl_2$ solution. Introducing the numerical values, the equation finally takes the form

$$\log \gamma_1 = 11.27E + (7.84695 - 10) - \log m_1$$

Taking the activity coefficients at round molal concentrations and comparing the values obtained with those of Lucasse, it is seen that they are in excellent agreement up to 1 M.

---

[7] Neuhausen, THIS JOURNAL, 44, 1945 (1922).

TABLE II

ACTIVITY COEFFICIENTS

m	(Obs.)	(Lucasse)	*m*	(Obs.)	(Lucasse)
0.01	(0.716)	(0.716)	0.20	0.481	0.480
.02	.655	.655	.50	.502	.499
.05	.567	.569	.70	.560	.560
.07	.539	.541	1.00	.685	.709
.10	.517	.516	2.00	1.150	1.521

The Determination of Activity Coefficients of Calcium Ions.—The problem of determining individual *ionic* activities by electromotive-force measurements involves the determination of liquid junction potentials, and although these potentials can be reduced to small values, they are not known with certainty. While individual ionic activities are of less value from the thermodynamic point of view than the activities of the ionized salts, they are of great importance in many biological and chemical fields where specific ion effects are considered.

There also exists the problem of determining a reference activity, since in working with amalgam electrodes it is difficult to extend the dilution sufficiently in order to take a_1 to be very small. However, in the concentration range studied (0.001–0.01 M) one can calculate the value of a reference activity by employing the equation developed by Debye and Hückel. The limiting expression for the activity coefficient of an ion in aqueous solution at 25° is $-\log_{10} \gamma = 0.505z^2\sqrt{\mu}$, where γ is the activity coefficient, z the valence of the ion, and μ the ionic strength. Experiments have shown that this equation applies at least approximately up to an ionic strength of 0.01. The ion activity, a, may be obtained from the relation $a = \gamma c$, where c is the stoichiometrical concentration. In this investigation these equations have been employed in calculating the value of the reference activity.

Drucker and Luft[5] attempted to determine the ionic activity of calcium in solutions of calcium sulfate but they stated that the limited solubility of the salt made accurate measurements impossible. As yet no one has attempted to work with amalgam electrodes in dilute solutions, possibly because of the fact that such measurements have been considered to be unreliable. The work of Allmand and Polack[8] on the sodium electrode has been criticized by Michaelis and Kawai[9] who claim that in dilute solutions the electrode functions as a mixed hydrogen and sodium electrode. Allmand and Polack made but very few determinations with dilute solutions, the most dilute being 0.01 molal.

In the course of developing an electrode suitable for use with dilute solutions, preliminary studies indicated the following facts. (1) A single electrode is preferable because double dropping electrodes are very difficult

---

[8] Allmand and Polack, J. Chem. Soc., 115, 1020 (1919).

[9] Michaelis and Kawai, *Biochem. Z.*, 163, 1 (1925).

to adjust properly. (2) There is an optimum amalgam concentration for a definite range of solution concentration. **(3)** The effect of electrode surface area is to be considered. (4) The solutions must be air free. (5) Small particles must be kept from depositing on the electrode surface, as they cause the rapid decomposition of the amalgam.

Experimental Procedure

A high grade of calcium sulfate was repeatedly shaken with conductivity water and filtered. The resulting paste was then used in making up the saturated solution.

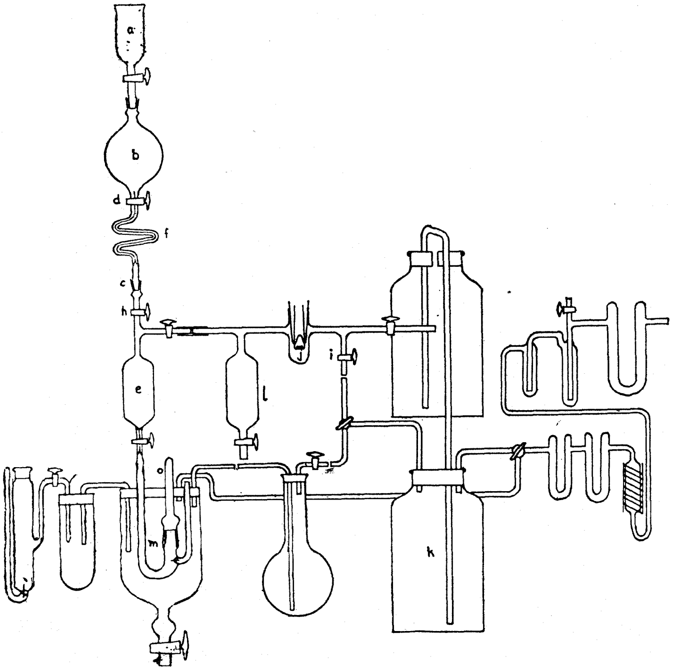


Fig. 1.—Apparatus for calcium electrode,

Other calcium salts used were listed as chemically pure and free from heavy metals. The solutions were made up accurately by weight on the molal basis.

In this part of the investigation the thermostat was discarded in order to facilitate manipulation of the apparatus. The temperature of the room was fairly constant, varying from 23.5–25°, and the errors from temperature fluctuations were less than other errors of measurement.

Commercial hydrogen from a tank was purified by passing it through solid potassium hydroxide, neutral permariganate solution, platinized asbestos at 300°, calcium chloride and phosphorus peatoxide.

The saturated calomel electrode was prepared using pure mercury, mercurous chloride and recrystallized potassium chloride. The bridge was made of saturated potassium chloride in agar-agar.

The apparatus employed is shown in Fig. 1. The entire system was first evacuated, then hydrogen from k was allowed to enter the system. Next a weighed quantity of metallic calcium was introduced into b and the apparatus again evacuated, and a weighed amount of mercury was allowed to flow into b from a. That part of the system which was above the ground-glass joint c was removed and the calcium was shaken with mercury to effect amalgamation. The apparatus was then reassembled and the system below the stopcock d was repeatedly evacuated and flushed out with hydrogen and finally evacuated. The stopcock d was opened and the amalgam allowed to flow from b into the reservoir e through the capillary filter f, which removed any oxide impurities. The stopcock h was then closed and pure hydrogen from k allowed to enter the system through i, which was then closed. The compartment j contained phosphorus pentoxide and a platinum glower to remove residual oxygen and water. The leveling bulb l was used to keep a pressure of hydrogen over the amalgam. The electrode m was fitted with a close-fitting cap o which was removed after the solution was introduced into the cell. With this type of apparatus the amalgam concentration and the electrode surface area were studied. For a solution concentration range of 0.02–0.001 M an amalgam concentration of 0.005–0.015% by weight was found to be satisfactory,

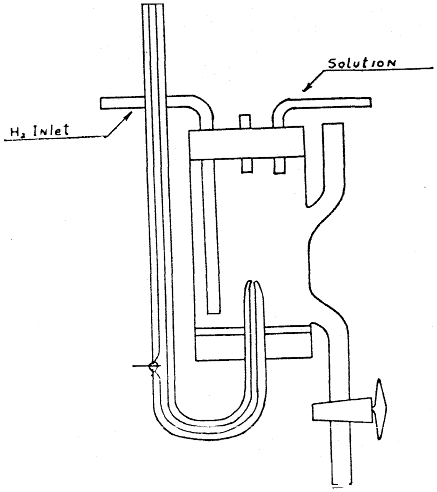


Fig. 2.—Final form of dropping electrode for calcium amalgam.

The first electrode studied was 15 mm. in diameter. In an attempt to measure the potential of an amalgam against a saturated solution of calcium sulfate, large voltage fluctuations were observed due to the decomposition of the amalgam at the surface. The second electrode was 9 mm. in diameter and was equipped with a rotating stirrer which not only agitated the solution but constantly scraped the surface of the amalgam. It was hoped that with this apparatus the solid particles of calcium hydroxide would be removed and the decomposition retarded, but the results were still erratic. Considerably better results were obtained with an electrode 4 mm. in diameter.

The final electrode is shown in Fig. 2. It was of the capillary type with a 1-mm. opening and was used in the experiments recorded in the tables. The stopper in the bottom of the cell was thickly coated with paraffin and inserted at such an angle as to insure the complete removal of the amalgam as it dropped off the tip of the capillary. Before a series of determinations was begun the tip of the capillary was filled with paraffin oil. This procedure was quite necessary as in the absence of the oil the electrode tip very soon became clogged on account of the accumulation of solid calcium hydroxide, necessitating the cleaning of the apparatus. The hydrogen inlet tube served to keep an atmosphere of hydrogen above the solution in the cell and also to agitate the solution during the operation of the electrode.

An inspection of the following tables shows that fairly accurate values of the activity coefficients may be obtained if the electrode surface area is small so that catalytic decomposition of the amalgam by particles of calcium hydroxide is minimized.

For a concentration cell with liquid junction the electromotive force and activity are related according to the following equation

$$E = E_1 - E_2 = \frac{RT}{NF} \ln \frac{a_1}{a_2}$$

or, substituting numerical values

$$E_1 - E_2 = 0.0295(\log \gamma_1 c_1 - \log \gamma_2 c_2)$$

The value of γ_1 is obtained from the Debye–Hückel equation. To illustrate the method of obtaining $-\log \gamma_2$, a calculation is carried out below using data from Table V.

$c_1 = 0.0015$ $c_2 = 0.0031$

$E_1 = 2.2335$ $E_2 = 2.2267$

$\log \gamma_1 = -0.158$ $\log \gamma_1 c_1 = -2.980$

Substituting these values in the above equation, $-\log \gamma_2 = 0.240$.

Results

All of the results have been calculated for the hypothetical cells Ca_xHg | c_1Ca^{++} | Satd. KCl in agar-agar | c_2Ca^{++} | Ca_xHg.

The amalgam contained 0.012% of calcium in all cases except in Tables V and VIII, where it contained 0.015%.

TABLE III

ACTIVITY COEFFICIENTS OF CALCIUM IONS CALCULATED FROM E.M.F. OF A CALCIUM AMALGAM ELECTRODE, TAKING FOR REFERENCE THE ACTIVITY IN A DILUTE SOLUTION AS CALCULATED FROM THE DEBYE–HÜCKEL EQUATION

CALCIUM SULFATE. t = 23.2°

M	E	ΔE	$-\log \gamma$ (calcd.)	$-\log \gamma$ (obs.)
0.0153	2.1853	0.0107	0.501	0.481
.0153	2.1853	.0107	.501	.481
.0077	2.1907	.0053	.343	.363
.0077	2.1905	.0055	.343	.353
.0038	2.1960	.0000	.250	Ref.
.0038	2.1957	.0003	.250	Ref.
.0038	2.1960	.0000	.250	Ref.

TABLE IV

CALCIUM SULFATE. t = 23.8°

M	E	ΔE	$-\log \gamma$ (calcd.)	$-\log \gamma$ (obs.)
0.0153	2.2119	0.0203	0.501	0.479
.0153	2.2121	.0201	.501	.480
.0092	2.2174	.0148	.388	.442
.0092	2.2173	.0149	.388	.439
.0015	2.2320	.0002	.158	Ref.
.0015	2.2322	.0000	.158	Ref.

TABLE V

CALCIUM SULFATE. t = 24.2°

M	E	AE	−Log γ (calcd.)	−Log γ (obs.)	
0.0153	2.2135	0.0203	0.501	0.479	0.481
.0122	2.2162	.0176	.446	.469	.483
.0092	2.2172	.0166	.388	.382	.391
.0061	2.2196	.0142	.315	.286	.296
.0031	2.2267	.0070	.224	.244	.240
.0015	2.2335	.0000	.158	Ref.	Ref.

TABLE VI

CALCIUM LACTATE. t = 25.0°

M	E	AE	−Log γ (calcd.)	−Log γ (obs.)	
0.010	2.2105	0.0086	0.349	0.325	0.332
.008	2.2128	.0063	.312	.313	.313
.006	2.2157	.0034	.271	.284	.278
.004	2.2191	.0000	.221	Ref.	Ref.
.002	2.2254	− .0063	.155	.139	.124

TABLE VII

CALCIUM HYDROXIDE. t = 24.0°

M	E	AE	−Log γ (calcd.)	−Log γ (obs.)	
0.0219	2.2053	0.0155	0.517	0.405	0.377
.0153	2.2113	.0095	.432	.413	.416
.0110	2.2135	.0073	.366	.366	.368
.0044	2.2208	.0000	.232	Ref.	Ref.
.0022	2.2266	− .0058	.165	.119	.....

TABLE VIII

CALCIUM CHLORIDE. t = 25.0°

M	E	AE	−Log γ (calcd.)	−Log γ (obs.)	
0.0604	2.1912	0.0288	...	0.464	0.484
.0483	2.1927	.0273	...	.414	.....
.0362	2.1985	.0215	...	.483	.481
.0242	2.2023	.0177	...	.442	.439
.0120	2.2091	.0109	0.385	.367	.366
.0085	2.2130	.0070	.322	.350	.355
.0060	2.2159	.0041	.271	.292	.286
.0036	2.2200	.0000	.216	Ref.	Ref.
.0012	2.2303	− .0103	.121	.087	.098

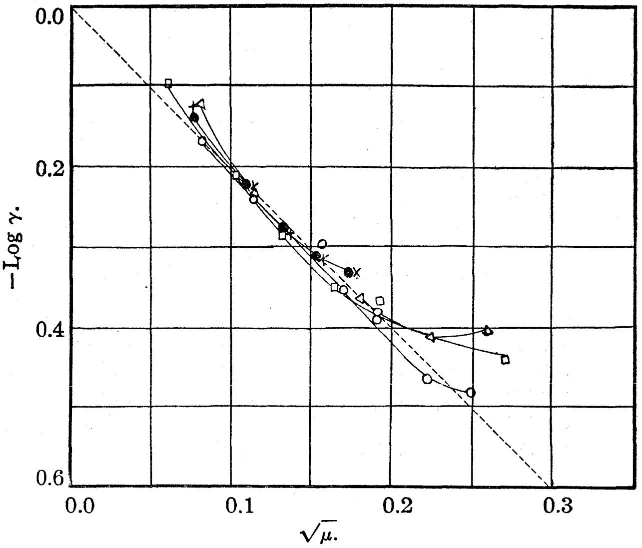
TABLE IX

CALCIUM ACETATE. t = 23.0°

M	E	AE	−Log γ (calcd.)	−Log γ (obs.)	
0.010	2.2105	0.0086	0.349	0.328	0.333
.008	2.2130	.0061	.312	.313	.313
.006	2.2157	.0034	.271	.284	.287
.004	2.2191	.0000	.221	Ref.	Ref.
.002	2.2252	− .0061	.155	.124	.120

In the preceding tables the value of the reference voltage was taken as the average of several determinations, and the results of duplicate experiments are given in the last two columns. In most cases the reference electrode was taken as the next to the most dilute solution rather than the most dilute solution because the experimental errors in the latter are larger.

The Debye–Huckel equation gives a straight line if $-\log \gamma$ is plotted as ordinates and the $\sqrt{\mu}$ as abscissas, as shown by the dotted line of Fig. **3.** Fig. **3** also contains the experimental data for the five different calcium compounds.



○, Calcium sulfate; △, calcium hydroxide; □, calcium chloride; ●, calcium lactate; X, calcium acetate.

Fig. 3.—Graph showing the relation between the activity coefficient of calcium ions and the ionic strength.

While the equation is a limiting expression and valid only up to the region of an ionic strength of 0.01 (or $\sqrt{\mu} = 0.1$) it may be employed as a first approximation in the region of the concentration studied. The curves obtained for the calcium salts deviate from the theoretical line, the deviations being larger at the higher ionic strength due to the failure of the simple theoretical equation in this region. No attempt is made here to test the validity of the Debye–Hückel expression but it is employed merely as a first approximation to which the experimental data may be compared. The exact curves are probably not significant because the experimental errors are large, but it is seen that they fall fairly close to the Debye–Huckel line. The deviations in the case of the most dilute solutions **may** probably be attributed to experimental difficulties in this region.

The Effect of Cations on the Potential of the Calcium Electrode.—Electromotive-force determinations of aqueous solutions of calcium salts against calcium amalgam have shown that the electrode is reliable in a concentration of calcium ions comparable to that contained in most physiological systems. The possible application of the calcium electrode to biological problems is at once suggested providing that the potential of the electrode is not seriously disturbed by other electrolytes or proteins present in such solutions.

Neuhausen[10] studied the effect of gelatin and various electrolytes on the reliability of the sodium electrode. From the results of a series of experiments he concluded that the addition of other electrolytes, in general, did not affect the potential of the electrode. To test this point in regard to the calcium electrode a small amount of another electrolyte was added to a solution of calcium sulfate and the effect on the potential was observed. The results of such a series of experiments are contained in Table X.

TABLE X

THE INFLUENCE OF ADDED ELECTROLYTES ON THE POTENTIAL OF A CALCIUM AMALGAM ELECTRODE

Amalgam = 0.012%. t = 23.8°

$CaSO_4$, *M*	Electrolyte added, *M* = 0.002	*E*	Δ*E*
0.0074	None	2.2186	0.0000
.0074	K_2SO_4	2.1936	.0250
.0074	Na_2SO_4	2.1758	.0428
.0074	$(NH_4)_2SO_4$	2.1583	.0603
.0074	$CuSO_4$	2.0089	.2097
.0074	$FeSO_4$	1.6123	.6063
.0074	Oxalic acid	1.9774	.2412
.0074	Tartaric acid	2.1313	.0873
.0074	$ZnSO_4$	2.1878	.0308
.0074	None	2.2185	.0000

In every case the potential of the electrode was lowered, probably on account of the formation of a mixed amalgam electrode. In the case of iron and copper ions it is likely that the amalgam decomposed rather rapidly. The potassium and sodium ions entered the amalgam and replaced calcium to a certain extent. This replacement is opposed to the normal positions in the electromotive-force series, but the difference between the potential of the sodium or potassium electrode and the calcium electrode is so small that a high concentration of sodium or potassium ions can replace a small number of calcium atoms.[11]

In order to determine if a similar effect can be observed in the case of a physiological solution containing other cations in addition to calcium

---

[10] Neuhausen, THIS JOURNAL, 44, 1445 (1922).

[11] Compare G. McP. Smith, *ibid.*, 27, 540 (1905), and later communications.

ions, a series of samples of fresh dog's blood was prepared. In the following table are contained the results of the determination of the electromotive force of a calcium amalgam against the blood samples. The author is indebted to Professor W. J. Meek of this University for help in these experiments.

TABLE XI

POTENTIALS OF A CALCIUM AMALGAM ELECTRODE IN BLOOD

$t = 25°$

Sample	Treatment	E
0.0153 M $CaSO_4$	....	1.9543
Blood	Hirudin added	1.7834
Blood	Oxalated	1.8095
Blood	Whipped	1.8112
Plasma	Centrifuged	1.7660
Blood	Whipped	1.8134
0.0153 M $CaSO_4$	....	1.9537

While the absolute values of the electromotive force are not exact, the data show conclusively the impossibility of applying the calcium electrode in this way to the determination of the calcium-ion concentration in blood or any solution containing cations other than calcium. The lower potentials with blood correspond to an impossibly high concentration of calcium.

It had been hoped that a relation would be found between the effect of various materials on the coagulation of blood and on the calcium-ion activity, but no conclusion can be drawn on account of the complication of other ions.

The Effect of Proteins on the Potential of the Calcium Electrode.—Neuhausen[10] reported that the addition of isoelectric gelatin to solutions containing sodium ions produced no observable effect on the reliability of the sodium electrode. For this reason it was thought that the calcium electrode might be applied in studying calcium proteinate systems.

One hundred grams of 8% isoelectric gelatin was covered with 600 cc. of air-free, saturated calcium hydroxide solution. The system was then immersed in ice water and allowed to stand for one hundred hours. The liquid outside the gelatin was poured off and the gelatin washed with ice water.

Approximately ten g. of Merck's soluble crystallized egg albumin was added to 400 cc. of an air-free saturated calcium hydroxide solution. The mixture was placed in a shaking machine and the shaking continued for a period of seven hours. During this time a slow stream of pure hydrogen was allowed to bubble through the solution. Solutions of calcium caseinate were prepared in a similar manner. The results of electromotive-force determinations of calcium amalgam against solutions of calcium proteinate are given in the following tables.

TABLE XII
INFLUENCE OF GELATIN

Solution	E	$a_{Ca^{++}}$
$Ca(OH)_2$, 0.0074 M	2.2215	0.0046
$Ca(OH)_2$, 0.0074 M	2.2214	.0046
$Ca(OH)_2$ filtrate	2.1870	.0676
$Ca(OH)_2$ filtrate	2.1872	.0676
Ca gelatinate solution	2.1557	.0746
Ca gelatinate solution	2.1560	.0746

TABLE XIII
INFLUENCE OF PROTEINS

$X = 0.015\%$. $t = 24''$

Solution	Concn. of calcium	E	ΔE
Ca albuminate	0.0219	1.9986	0.2210
Ca albuminate	.0044	2.0861	.1335
$Ca(OH)_2$	.0219	2.2196	.0000
$CaCl_2$ + albumin	.0604	1.8416	.3514
$CaCl_2$ + albumin	.0121	1.9532	.2398
$CaCl_2$	.0604	2.1930	.0000
1 cc. $CaCl_2$ + Albumin + 49 cc. $Ca(OH)_2$	.030	2.2055	.0058
49 cc. $Ca(OH)_2$ + 1 cc. $CaCl_2$	.030	2.1113	.0000
Ca caseinate	.0219	1.8100	.4106
1 cc. Ca caseinate + 49 cc. $Ca(OH)_2$	.0223	2.2120	.0086
$Ca(OH)_2$	.0219	2.2206	.0000

The data clearly show that in a solution containing 0.02% or even a smaller amount of protein the reliability of the electrode is destroyed, for the values of "a" and ΔE correspond to an impossibly high concentration of calcium ions.

The alteration in the potential must be due to a change which takes place at the surface of the electrode. To account for this effect the following explanation is advanced. Because of a tendency of the protein to form a film on a metallic surface a coating is formed on the surface of the electrode. This film prevents the ordinary electrode equilibrium from taking place and results in the building up of a large ionic concentration inside the film. Experiments conducted with other metallic electrodes in protein solutions indicated the plausibility of this hypothesis. The results also suggest the reason for the failure of other investigators to develop a technique applicable to the study of calcium solutions containing protein.

The author desires to acknowledge the help given by Professor Farrington Daniels, under whose direction this investigation has been carried out.

Summary

1. Values of the activity coefficients of calcium chloride are given from **0.01–3.3** molal. The values up to a concentration of 1.0 molal agree very well with those obtained by Lucasse.

2. A technique and an apparatus suitable for the determination of the activity coefficients of calcium ions have been developed.

3. Values of the activity coefficients of calcium ions in aqueous solution for five calcium salts have been determined from 0.01-0.001 molal.

4. The investigation has revealed apparently insurmountable difficulties in using the calcium electrode for the determination of calcium-ion activities in physiological solutions. The potential is lowered by the presence of cations, either above or below calcium in the electromotive-force series. The potential is lowered also by the presence of protein.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LABORATORY OF MICRO-ANALYSIS, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

MICRO-POTENTIOMETRIC DETERMINATION OF REDUCING CARBOHYDRATES

BY JOSEPH B. NIEDERL AND RALPH H. MÜLLER

RECEIVED SEPTEMBER 24, 1928 PUBLISHED MAY 6, 1929

Introduction

Of the various types of methods in existence for the micro-determination of reducing sugars, the copper reduction method with its various modifications is used most extensively.[1]

It has been shown by Daggett, Campbell and Whitman[2] that reducing sugars can be determined potentiometrically. The purpose of this communication is to show that micro-analytical determination can be made by this method and that the method may be simplified by the use of a more convenient electrode than the calomel electrode employed by these authors. The more important carbohydrates have been studied and their reduction values ascertained. One method (semi-micro) permits the determination of 3 to 5 mg. with an accuracy of about ±1%, while the other (micro) permits a quantitative determination of as little as 0.05 mg. of reducing carbohydrates.

[1] (a) I. Bang, *Biochem. Z.*, 87, 27, 248, 264 (1918); (b) 88, 92, 344 (1918); (c) H. MacLean, *J. Physiol.*, 50, 168 (1916); (d) *Biochem. J.*, 13, 135 (1919); (e) P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, 45, 349, 365 (1921); (f) A. Kowarsky, *Deut. med. Wochschr.*, 45, 188 (1919); (g) E. Mislowitzer, *Biochem. Z.*, 67, 168, 217 (1916); (h) S. Zisa, *Chem. Zentr.*, [I] 2611 (1926); (i) S. Rosenthaler, *Arch. Pharm.*, 263, 518 (1926); (j) G. Fontes and L. Thivolle, *Compt. rend. soc. biol.*, 84, 669 (1921); (k) O. Folin and Hsien Wu, *J. Biol. Chem.*, 38, 106 (1920); (l) 41, 367 (1920); (m) O. Folin and H. Berglund, *ibid.*, 51, 209 (1922); (n) V. E. Rothberg and F. A. Evans, *ibid.*, 58, 435, 443 (1922); (o) S. Morgulis and co-workers, *Chem. Zentr.*, [IV] 635 (1923); (p) S. R. Benedict, *J. Biol. Chem.*, 64, 207 (1926); (q) 68, 759 (1926); (r) L. Lorber, *Biochem. Z.*, 158, 158, 205 (1925); (s) E. Komm, Z. *angew. Chem.*, 38, 1094 (1926); (t) Goiffon and Nepveux, *Compt. rend. soc. biol.*, 83, 121 (1920); (u) D. Charnass, "Biol. Arbeitsmethoden," Abt. IV, T. 4, p. 1179.

[2] Daggett, Campbell and Whitman, THIS JOURNAL, 45, 1043 (1923).

Apparatus.—The apparatus consisted of two vessels filled with Fehling's solution of the same concentrations. Platinum electrodes were immersed in each vessel, the two vessels being connected by an agar agar–potassium chloride bridge. One vessel was heated and the sugar solution added slowly from a buret. The difference in the potential of the electrodes was followed by means of a Leeds and Northrup Type K potentiometer. The Hildebrand[3] arrangement was also used successfully.

Figure 1 illustrates this arrangement as employed in the micro-determination. The vessels in this case were small pyrex tubes. The bridge consisted of a capillary tube of 1 mm. outside diameter, filled with agar agar–potassium chloride gel.

Experimental Part

Three to 5 mg. of the substance is weighed accurately on a micro-analytical balance down to 0.001 mg. (Kuhlmann balance; Becker's micro-analytical balance might also be used) and dissolved in distilled water, one cc. for each mg. The solution is put in the micro-buret. To each of the two vessels 1 cc. of Fehling's solution containing one mg. of copper per cc. is added. **A** reading is now taken on the potentiometer. Then the Fehling's solution in container **A** is heated to boiling and a reading taken again.

A preliminary titration is first carried out as follows: 0.1 cc. of the solution containing the carbohydrate is added from the buret, the mixture boiled and a reading taken again. These additions are continued until 1.2 cc. has been used.

In the region of the end-point the increase in potential is very rapid. The maximum value of millivolts per 0.01 cc. marks the end-point.

The Fehling's solution used was prepared as follows: 3.95 g. of $CuSO_4 \cdot 5H_2O$ in 500 cc. of water, and 19.75 g. of sodium potassium tartrate and 7.40 g. of sodium hydroxide in 500 cc. of water.

The actual determination is carried out in the same way as the previous one, using larger amounts until the end-point is approached. From this point small amounts, not exceeding 0.02 cc., are added and after boiling readings are taken. This is continued over the range ascertained in the first trial.

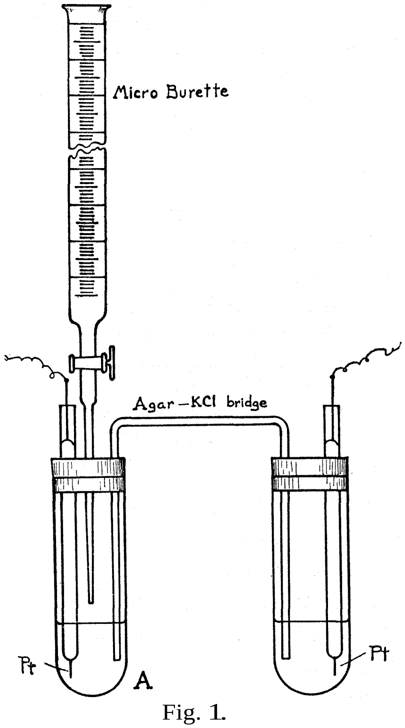


Fig. 1.

The change in potential in the vicinity of the end-point was always very large, enabling one to determine it without difficulty. The actual values of the potentials, however, were not as highly reproducible, owing to the fact that the reaction was

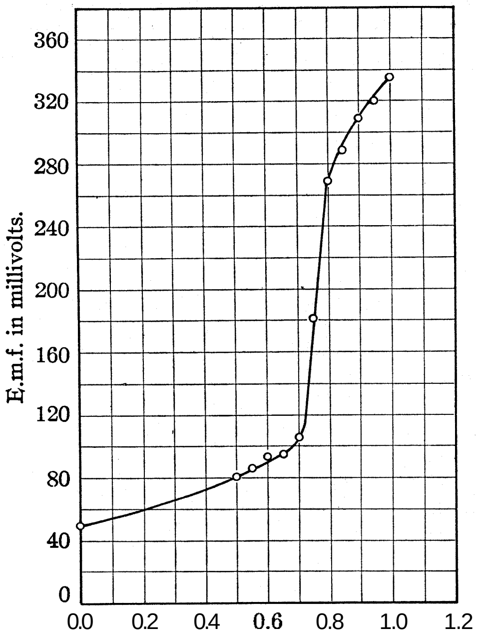
---

[3] Hildebrand, This Journal, 35, 847 (1913).

carried out in an alkaline medium and no particular precautions were taken for constant temperature. A typical titration curve is reproduced in Fig. 2.

For those cases in which less than four mg. is available, the material is weighed out according to **Pregl**,[4] and placed directly in the titrating vessel. Then Fehling's solution is added as before, boiled and readings are taken on the potentiometer.

The titration itself, however, is completed with standard glucose solution (1 mg. in 1 cc.) in the manner given. The difference in the volume necessary for the end-point gives the amount of carbohydrate present. Naturally a solution (1 cc.) free from other reducing substances might also be used instead of the solids.



Sugar solution (concn., 1 mg. in 1 cc.), cc.

Fig. 2.

Discussion of Results

Under the experimental conditions outlined above, the following empirical standard values were obtained.

1 Mg. of Copper

Sugar	Mg.
d-Glucose	0.635
d-Mannose	.638
d-Galactose	.770
d-Fructose	.679
Maltose	1.019
Lactose	.884
Sucrose (inverted)	.657

1 Mg. of Sugar

	Cu, mg.
d-Glucose	1.575
d-Mannose	1.567
d-Galactose	1.298
d-Fructose	1.472
Maltose	0.981
Lactose	.884
Sucrose (inverted)	1.522

Each of these empirical standard values represents the average of at least six determinations.

Some of the results as obtained by this method by various individuals are given below. The Fehling's solution contained 1 mg. of copper in 1 cc. All the sugar solutions used also contained 1 mg. of reducing carbohydrate in 1 cc. The materials used were "Kahlbaum" chemicals of highest purity.

Since the reducing power of the various carbohydrates changes with the reaction conditions, such as concentration, temperature and oxidizing reagent, the foregoing values do not check absolutely with the figures given in the literature and obtained under different conditions, although

---

[4] Pregl, "Quantitative Organic Micro-analysis," P. Blakiston's Sons and Co., Philadelphia, 1924.

1 Mg. sample	Cu, mg.	Average	1 Mg. sample	Cu, mg.	Average
d-Glucose	0.630–0 660	0.645	d-Fructose	0 675–0.700	0.687
Standard value,	.630– .640	.635	Standard value,	.650– .680	.665
0.635	.630	.630	0 679	.675– .700	.687
	.630	.630	Maltose	1.050–1.100	1.075
	.630	.630	Standard value,	1.000–i.050	1 025
	.620– .640	.630	1.019	1.000–1.025	1.013
	,630–.650	.640		1.000–1.030	1.015
	.625– .650	.638		1.000–1.050	1 025
d-Mannose	0.625–0.650	0.638	Lactose	0.850–0.900	0.875
Standard value,	.625– 650	.638	Standard value,	.850– .900	875
0.638	.625– .650	.638	0.884	.880– .900	.890
	.600– .700	.650		.880– .900	.890
	625– .650	.638		.880– .900	.890
d-Galactose	0.750–0.800	0.775	Sucrose (inverted)	0.650–0.675	0 663
Standard value,	,770– 800	.785	Standard value,	.650	.650
0.770	,750–.780	.765	0.657	.650– .675	,663
	.750– .780	.765			
	.750– 775	.760			

they correspond in the order of the reducing power with those obtained by related methods. The comparison is as follows.

Order of red. power	Potent. titr.	E. Wein	Lewis Benedict	Folin–Wu	Fehling	Knapp	Sachsse
1	Glucose	Glucose	Glucose	Glucose	Glucose	Fructose	Fructose
2	Sucrose	Sucrose			Sucrose	Sucrose	Sucrose
3	Mannose		Mannose	Fructose			
4	Fructose		Fructose	Galactose	Galactose	Glucose	Glucose
5	Galactose		Galactose	Mannose	Fructose	Galactose	Galactose
6	Lactose	Lactose	Lactose	Lactose	Lactose	Lactose	Lactose
7	Maltose	Maltose	Maltose	Maltose	Maltose	Maltose	Maltose

In carrying out numerous titrations by the method set forth herein where the Fehling's solution is just brought to boiling after each addition of the carbohydrate solution, no appreciable differences in the results were noted, whether the solution was boiled up 5, 6, 7 or 8 consecutive times. Perhaps in such diluted solutions the time factor no longer is of marked influence.

Since the various sugars have different standard values, it is evident that in a pure sample also the qualitative nature of the carbohydrate may be ascertained by comparing the titration curve obtained with the standards. For example, if a pure sample weighing 1 mg. consumes **0.981** mg. of copper it can only be maltose, etc.

The authors desire also to thank Mr. Nathan Ambinder for carrying out a large number of titrations.

Summary

Micro-potentiometric methods for the quantitative determination of reducing carbohydrates have been described.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE JOHNS HOPKINS UNIVERSITY]

CRITICAL TEMPERATURE MEASUREMENTS ON CARBON DIOXIDE IN SMALL CAPILLARIES[1]

BY HARVEY THOMAS KENNEDY

RECEIVED OCTOBER 10, 1928 PUBLISHED MAY 6, 1929

Patrick and McGavack[2] have established the relation between the quantity of gas adsorbed by silica gel and the equilibrium pressure, as follows

$$V = K\left(\frac{\sigma P}{P_0}\right)^{1/n}$$

where V is the volume of liquefied gas at the prevailing temperature and pressure, σ the corresponding surface tension, P is the equilibrium pressure, P_0 is the ordinary saturation pressure and K and n are constants. This equation has been used to correlate measurements of adsorption in silica gel with the vapor pressures of sulfur dioxide and ammonia by Patrick and Davidheiser,[3] of butane by Patrick and Long[4] and of nitrous oxide and carbon dioxide by Patrick, Preston and Owens.[5] The latter writers made measurements of adsorption both above and below the critical temperature and concluded that liquid exists in the pores of the adsorbant above the critical temperature, as ordinarily measured in large tubes. Thus they believe that liquid carbon dioxide exists in the pores of silica gel at 40°, about 9° higher than the previously reported critical temperature.

While it is perhaps impossible to test this hypothesis directly, that is, by actual observation of a liquid phase within the fine pores of an adsorbent, it was thought that if the hypothesis were in accord with the facts, some increase in critical temperature should be observed in very fine glass capillaries, even though the diameters of the capillaries were many times those of the finest pores in silica gel. The work here described was undertaken largely to determine what relation, if any, exists between the diameter of small capillaries and the critical temperature of material measured in them.

Carbon dioxide was chosen for this work because its critical point is conveniently near to room temperature and because it is easily obtained in a state of high purity.

The first attempt to determine the effect which diameter of capillary had on the critical temperature consisted in the construction of the apparatus shown in Fig. 1 which contains carbon dioxide adjusted to critical volume. When the temperature is raised slowly from slightly below the

---

[1] Dissertation submitted to the Board of University Studies of Johns Hopkins University, in conformity with the requirements for a degree of Doctor of Philosophy.

[2] McGavack and Patrick, THIS JOURNAL, 42, 946 (1920).

[3] Davidheiser and Patrick, *ibid.*, 44, 1 (1922).

[4] Patrick and Long, J. *Phys.* Chem., 29, 336 (1925).

[5] Patrick, Preston and Owens, *ibid.*, 29, 421 (1925).

critical to slightly above, it was expected, if the diminishing diameter had the effect of raising the critical temperature, that the meniscus would appear in the tube D and slowly move from the upper and larger end to the lower and smaller end. Conversely, as the temperature is lowered, the opposite motion should be observed.

As impurities in the carbon dioxide might give the same effect as described above, without the diameter itself having any effect, the greatest care was exercised in preparation and purification.[6]

Figure 2 shows diagrammatically the apparatus by which the carbon dioxide was further purified and conducted into the tube shown in Fig. 1 by multiple sublimation.

Before the purification was completed, no measurable pressure was indicated on the McLeod gage when liquid air was placed under either I or J, and the sublimation into it completed, the stopcock O being closed.

The behavior of the meniscus was then observed by placing the tube D before a microscope, the optical axis of which was horizontal, and which was so arranged that it could be moved up and down, thus allowing the tube to be viewed throughout its length. A mercury thermometer graduated in 0.01° was placed at the side of the tube D, and the room temperature was varied very slowly and regularly by means of a large fan and gas flames placed a considerable distance from the apparatus.

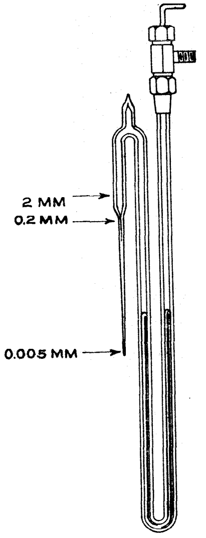


Fig. 1.

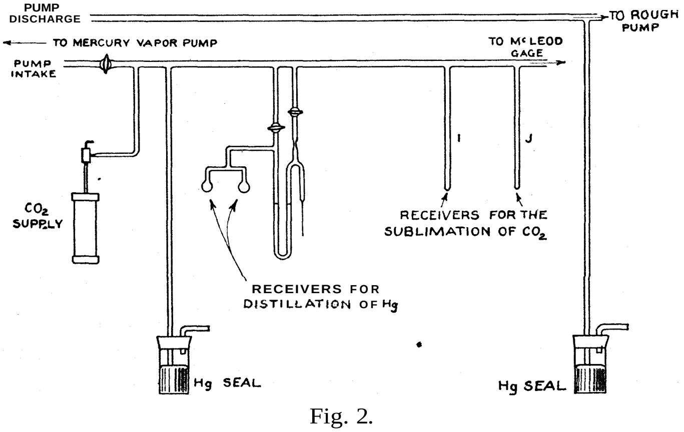


Fig. 2.

The result predicted by the hypothesis explained at the beginning of this paper, namely, that the meniscus should move downward in the tube D as

---

[6] For a detailed description of the generation and purification of the carbon dioxide used in this investigation, see Meyers and Van Dusen, *Refrigerating Eng.*, 13, 180 (1926).

the temperature was raised, and vice versa, was not observed since no meniscus was observed in the small tube D at any time, although the temperature was raised above the critical and lowered many times, and various schemes of illumination tried.

It was then decided that the negative result obtained was not entirely conclusive. The meniscus, if present in the very fine tube would be difficult to see, and great delicacy in temperature control might be necessary to hold it at any point in the tube for a long time. It was, therefore, decided to make determinations of the critical temperature of carbon dioxide in very fine capillaries of different diameters and to compare these values with those obtained in larger tubes.

To make and fill these tubes, essentially the same apparatus was used as is shown in Fig. 2, the fine tubes being made by heating the ends of tubes I and J, drawing out to the required internal diameter and, after filling, collapsing until adjusted to critical volume.

These small tubes were drawn as described for two reasons: first, the ratio of surface to volume in them was very great as compared to tubes in which critical temperatures have previously been determined, and small quantities of adsorbed gases on the glass walls would have a much greater effect; second, previous work has shown that the action of water on soft glass essentially changes its surface, and irregularities thus caused might interfere with observations of critical temperature. It is believed that with freshly drawn tubing, which has never been in contact with any gas except carbon dioxide of high purity, both of these difficulties are overcome.

The apparatus for the determination of the critical temperatures of carbon dioxide in the small tubes is shown in Fig. 3.

Temperature regulation was secured by the 40-watt lamp I, which was connected to a line the voltage of which could be varied in 11-volt steps. External resistance in series with the lamp was also provided so that fairly rapid or very slow rates of heating could be obtained. The lamp was surrounded with a section of a cone, made of black paper, with a disk of the same material on its top so perforated that the direct radiation from the lamp did not fall upon the contents of the Dewar tube.

Illumination was secured by a 200-watt tungsten lamp set beyond the Dewar tube at an angle of about 30° with the optical axis of the microscope. Between the Dewar tube and the lamp was placed a large bottle of water so as to shield the water in the Dewar from the heat from this source. It was found that the very small tube could best be observed by moving the microscope objective somewhat further away from the tube than the position corresponding to sharp focus and observing a greatly enlarged pattern formed only when an angle of approximately 30" existed between the optical axis of the microscope and the line from the lamp to the Dewar tube. In this pattern liquid and vapor were differentiated as light and dark bands, and could be clearly distinguished, especially when moving, in tubes so small that the two sides could be resolved only with difficulty with the magnifying power available.

A number 4 objective was used, the limitation imposed by the thickness of the wall of the Dewar preventing the use of one of higher magnifying power.

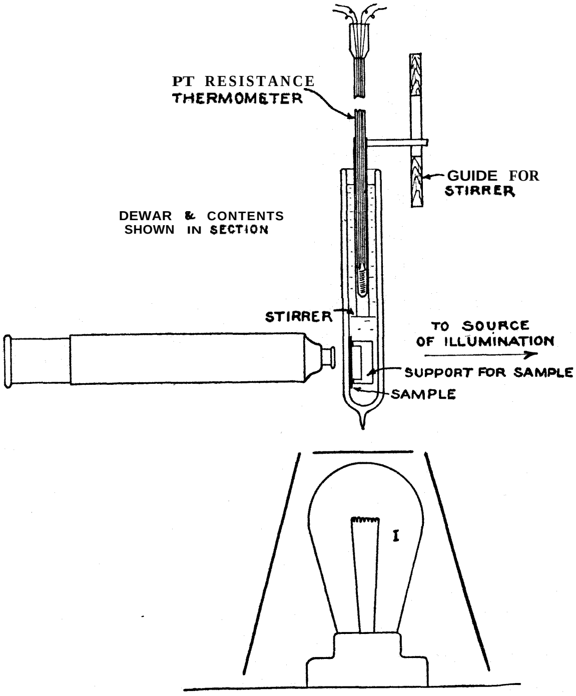


Fig. 3.

Determinations of critical temperatures were made on samples contained in two small capillary tubes whose internal diameters midway between the two ends were 0.004 and 0.060 mm., respectively, as measured microscopically and corrected for the magnifying power of the glass. Several determinations were also made on the 2-mm. tube shown in Fig. 1 and

TABLE I

RESULTS OF EXPERIMENTS

	Tube no.		
	1	2	3
Internal diameter, mm.	0.004	0.060	2.0
Approximate length, mm.	15	15	80
Meniscus appeared	30.96 30.95	30.96	30.96
	30.985 30.94	30.96	30.96
Average	30.96	30.96	30.96
Meniscus disappeared	30.95 30.94	30.95 30.95	30.96
	30.98 30.93	30.96 30.96	
Average	30.95	30.955	30.96

these values are tabulated here for comparison. Temperatures are recorded at which the meniscus first appeared as the temperature was falling, and at the highest temperature at which a meniscus was seen as the tubes were slowly heated.

It will be observed that while the reproducibility of results on tube No. 1 leaves much to be desired, the average of the temperatures at which the meniscus appears is the same for all the tubes, that is, 30.96". Similarly the meniscus disappears between 30.95 and 30.96°, taking average figures, for all of the tubes, regardless of size. Runs in which the temperatures changed more than 0.02° per minute are not tabulated above.

The temperature 30.96 * 0.01" as the critical point of carbon dioxide, measured as here described, appears to be the most probable result, independent of the diameter of the tube in which it is measured. Whether the independence of capillary diameter and critical temperature holds in tubes whose diameter is of the same order of magnitude as the finest pores in charcoal or other adsorbing material, is of course conjectural. What is here proved is that there is no effect exceeding 0.03" for tubes as small as 4 microns in diameter.

The above figure is also suggested as an accurate value for the critical temperature of carbon dioxide, and the method here described as one of unexcelled precision, although more laborious than methods previously described. The greatest precision is probably attained in tubes the internal diameter of which is about 60 microns. The precision attainable in small tubes illuminated as described arises from the fact that up to the critical temperatures a sharp meniscus is observed. As the critical point is reached, violent motion is observed, and within a few thousandths of a degree, the meniscus, still moving, disappears. No bands or fog, such as are observed in large tubes with the naked eye, are visible.

Comparing the value here reported with critical temperatures determined by the more recent investigators, it will be noted that the present value is, in general, low. Thus, Meyers and Van Dusen[6] set 31.1° as the best figure. Hein[7] obtained 30.97"; Cardoso and Bell,[8] 31.00"; Dorsman,[9] 31.10"; Bradley, Brown and Hale,[10] 31.26°; Onnes and Fabius,[11] 30.985°; Brinkmann,[12] 31.12°; Keesom[13] 30.98°, and von Wesendonck[14] considered

[7] Hein, *Z. physik. Chem.*, 86, 385 (1913–1914).

[8] Cardoso and Bell, *J. Phys. Chem.*, 10, 500 (1912).

[9] Dorsman, "Dissertation," Amsterdam, 1908.

[10] Bradley, Brown, and Hale, *Phys. Rev.*, 26, *470* (1908).

[11] Onnes and Fabius, *Verslag. Akad. Wetenschappen Amsterdam,* 44 (1907); *Comm. Phys. Lab. Univ. Leiden,* No. 98, 1907.

[12] Brinkmann, "Dissertation," Amsterdam, 1904.

[13] Keesom, *Verslag. Akad. Wetenschappen Amsterdam,* 321, 533, 616 (1903); *Comm. Phys. Lab. Univ. Leiden,* No. 88, 1903.

[14] Von Wesendonck, *Verh. deutsch. phys. Ges.*, *5,* 238 (1903).

the critical temperature indefinite within the range 30.95 to 31.7°. Among the results obtained previous to 1900, Andrews' value[15] of 30.92° is the lowest, all other temperatures recorded being 31.0" or higher.

The critical temperature, as used in this work, is the highest temperature at which a meniscus of sufficient sharpness to be seen in the field of a microscope when the material is examined by transmitted light can be observed. As the same results were obtained with an ordinary reading glass as with the microscope previously described, it is believed that this definition need not be amplified as regards magnification. It is suggested that the variation in critical temperatures as measured by the more modern workers in this field is due largely to the different criteria employed to define the critical point. Thus, when the 3-mm. tube used by Meyers and Van Dusen was examined by the author using transmitted light of high intensity[16] no meniscus that was entirely sharp was observed above 30.97". By reflected light, however, a wide band was observed up to 31.1°, and fog at temperatures above 31.11". Similarly, when the tube shown in Fig. 1 was observed by reflected light, a wide band was observed up to 31.04'. Observations on the band could not be repeated with satisfactory precision.

The selection of any one of the various physical phenomena which occur at the critical temperature as a means of defining this temperature precisely is necessarily somewhat arbitrary. Of the two phenomena described in this paper, namely, the appearance or disappearance of a band and the appearance or disappearance of the meniscus, the latter seems to be better adapted for practical definition of the critical temperature. It has been pointed out by Mr. C. H. Meyers,[17] however, that, due to the extreme compressibility of a substance in the critical region, a pressure gradient such as that due to gravity may cause a region of rapidly changing refractive index in a single-phase system, giving the appearance of a band which becomes sharper the nearer the temperature approaches the critical, as here defined.

This opportunity is taken to acknowledge with gratitude the encouragement and advice received from Dr. J. C. W. Frazer and Dr. W. A. Patrick, of the Department of Chemistry, Johns Hopkins University, whose guidance has made this work possible.

The kindness of Dr. H. C. Dickinson, Chief of the Heat and Power Division, Bureau of Standards, in making available to the writer much of the apparatus and materials used in this work, is gratefully acknowledged.

---

[15] Andrews, *Trans.* Roy. *Soc. London,* II, **159,** *575* (1869).

[16] The tube used by Meyers and Van Dusen was mounted on a solid backed board and could not be illuminated from directly behind. The meniscus was observed by so placing a 200-watt tungsten lamp that the line between the lamp and the observer's eye was nearly parallel to the board.

[17] Private communication.

To Mr. C. H. Meyers of the Bureau of Standards, especial credit is due for placing at the writer's disposal his specialized knowledge of critical temperature determinations, and for assistance freely given in cases where two observers were required.

Summary

The critical temperature of carbon dioxide has been measured in glass tubes ranging from 2 mm. to **0.004** mm. in diameter. The critical temperature was found to be independent of the size of the tube and 30.96° was taken as the most probable value. Large differences in critical point were found for different methods of illumination and depending on whether a sharp meniscus or diffuse band is taken as a criterion.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 194]

VOLUMETRIC DETERMINATION OF VANADIUM BY MEANS OF POTASSIUM IODATE

BY ERNEST H. SWIFT AND RAYMOND W. HOEPPEL

RECEIVED NOVEMBER 13, 1928 PUBLISHED MAY 6, 1929

Introduction

The advantages of the iodate method of volumetric analysis have been pointed out by Andrews[1] and Jamieson,[2] and more recently reviewed by Heisig.[3] Among these advantages are the ease with which a standard solution of potassium iodate is prepared and the stability of its solution. Not only can substances which reduce iodate in hydrochloric acid solution be titrated, but it has been shown by Andrews[1] that oxidizing agents, such as chromates and chlorates, which oxidize iodide and are not re-oxidized by iodine monochloride, can be determined by adding an excess of a standard solution of potassium iodide and then converting the iodine liberated and the excess of iodide to iodine monochloride by titration with iodate solution. It was to be expected that a similar determination of vanadium as vanadate could be made, provided a sufficiently high concentration of hydrochloric acid could be maintained during the titration with the iodate to prevent re-oxidation of the quadrivalent vanadium formed. The chemical reactions involved in such a process can be represented as follows

$$H_3VO_4 + HI + 2HCl = VOCl_2 + \tfrac{1}{2}I_2 + 3H_2O$$
$$2I_2 + HIO_3 + 5HCl = 5ICl + 3H_2O \text{ and}$$
$$2HI + HIO_3 + 3HCl = 3ICl + 3H_2O$$

---

[1] Andrews, *Z. anorg. Chem.*, 36, 83 (1903); THIS JOURNAL, 25, 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, 1926, p. 9.

[3] Heisig, THIS JOURNAL, 50, 1687 (1928).

Such a method would offer the advantages of not requiring a previous reduction of the vanadate, which is the most commonly occurring form of vanadium, and of determining vanadium in the presence of iron, arsenic and phosphate, substances commonly occurring with vanadium in its natural sources.

Preliminary determinations which gave promising results were carried out by Mr. T. G. Bernhardi in this Laboratory. A more detailed study of the method was then undertaken by the authors.

Substances and Solutions.—All chemicals used were of "analytical chemical" grade.

Ammonium metavanadate was used as the source of the vanadium. The solution was prepared by weighing out the solid, dissolving it in an equivalent amount of sodium carbonate solution and expelling the ammonia by boiling. The vanadate solution was then standardized by the iodimetric method, using the procedure recommended by Ramsey.[4] Three determinations gave the values 0.05215, 0.05217 and 0.05215 for the molal concentration of the solution.

The potassium iodate was tested for iodide with negative results. The solutions were prepared by weighing out the dried salt and dissolving it in the proper volume of water to make the resulting solutions 0.025 molal.

The potassium iodide solution was prepared from the same grade of salt and proved to be iodate-free. The salt was weighed out and dissolved, and the concentration was determined by titration with the iodate solution under the conditions of the method being used.

The Method of Analysis.—The general procedure was to pipet the vanadate solution into a 200-ml. or 400-ml. conical flask with a ground-glass stopper and then to add slowly to this, while cooling the flask with tap water, the volume of 12 molal hydrochloric acid necessary to give the final concentration of the acid which was desired. The hydrochloric acid used in most cases had previously had a slow current of carbon dioxide passed through it for fifteen to twenty minutes in order to remove most of the dissolved oxygen. Through the flask containing the acid and the vanadate was then passed over the solution for two to three minutes a vigorous current of carbon dioxide. Then 3 to 5 ml. of carbon tetrachloride and a measured excess of the standard potassium iodide solution were added, the flask was closed and allowed to stand for one to two minutes; the solution was titrated as rapidly as possible with the iodate solution until no more iodine color could be detected in the carbon tetrachloride.

Test Analyses: Effect of Acid Concentration and Presence of Air.—In Table I are shown the results obtained in titrating known quantities of vanadium in the presence of hydrochloric acid at different concentrations and under certain other variations of the conditions.

In each case 25 ml. of the standard potassium iodide solution was added, except in Expt. 18, where 50 ml. was taken. Two standard solutions of potassium iodide were used in the experiments, one solution being 0.05414 molal and the other 0.05404 molal. The volume of potassium iodate used in the titrations varied from 13.46 ml. in Expt. 1 to 28.08 ml. in Expt. 18.

It will be seen that when the final concentration of the hydrochloric acid is 6 molal or 7 molal the results are satisfactory. The average of the fifteen

---

[4] Ramsey, This Journal, 49, 1138 (1927).

TABLE I

TITRATION OF VANADIUM WITH IODATE AT VARIOUS ACID CONCENTRATIONS

Expt.	Vanadium taken, mg.	Final concn. of HCl, M	Vanadium found, mg.	Expt.	Vanadium taken, mg.	Final concn. of HCl, M	Vanadium found, mg.
1[a]	66.44	3.8	69.36	18	132.88	6.0	132.32
2"	66.44	3.8	66.91	19	26.58	6.0	26.66
3"	66.44	3.8	63.45	20	66.44	6.0	66.41
4"	66.44	3.8	65.99	21	66.44	6.0	66.36
5	66.44	3.7	63.60	22	66.44	6.0	66.16
6	66.44	3.8	65.99	23	66.44	6.0	66.21
7	66.44	3.9	66.61	24	26.58	6.0	26.71
8	66.44	3.8	65.08	25	26.58	6.0	26.66
9	66.44	3.8	64.72	26	26.58	6.0	25.74
10[a]	66.44	5.0	66.61	27	26.58	6.0	26.61
11[a]	66.44	5.0	66.81	28	26.58	6.0	26.25
12	66.44	5.0	66.10	29	26.58	6.0	26.10
13	66.44	5.0	66.20	30[c]	26.58	6.0	26.71
14[b]	66.44	6.0	66.45	31[c]	26.58	6.0	26.66
15	66.44	6.0	66.30	32"	66.44	7.0	66.47
16	66.44	6.0	66.16	33[c]	66.44	7.0	66.41
17[b]	66.44	6.0	66.30	34[c]	66.44	7.0	66.41

[a] Neither the hydrochloric acid nor the flask was swept out with carbon dioxide.

[b] The flask was not swept out with carbon dioxide.

[c] Carbon dioxide was passed through the flask with vanadate before adding hydrochloric acid.

analyses at 6.0 M (excluding Expts. 26–29 for the reasons given below) is 0.08% low, and the greatest deviation from the correct value is 0.43%.

When the hydrochloric acid is 5 molal the results are not so good; they are low where the air is excluded and high when it is present, the latter probably being due to slight re-oxidation of the quadrivalent vanadium. It will be noted that a difference of about 1% is caused by not excluding the oxygen of the air. This effect (of not excluding the air) is apparently larger than with the 6 molal acid. It seems remarkable that this effect is not greater, considering the larger deviation obtained by Ramsey[4] when he allowed vanadate and iodine to react without excluding the oxygen of the air at much lower concentration of acid than was present in these experiments, but the smaller excess of iodide here present probably decreases the oxygen error.

At the lowest concentration of the hydrochloric acid the results show still more variability. This may be attributed to two factors: partial re-oxidation of the vanadium to vanadate and insufficient concentration of the hydrochloric acid to prevent hydrolysis of the iodine monochloride; this concentration is at the minimum of 12% which Jamieson[2] states is necessary in order to eliminate this hydrolysis.

It may be mentioned that the acid concentration during the vanadate–iodide reaction varies from 7 to 10 molal, and that under these conditions the vanadium may be reduced below the quadrivalent state; but, so long as oxygen is excluded, this causes no error, since it is immediately re-oxidized upon addition of the iodate.

In Expts. 26–29 the solution of the vanadate was 10 molal in hydrochloric acid while being swept with carbon dioxide; subsequent tests above the surface of the solution with paper strips moistened with a solution of starch and potassium iodide showed that a slight amount of chlorine was formed even in a cold solution, thus accounting for the low results obtained. Under the same conditions when the hydrochloric acid was added after sweeping out the flask with carbon dioxide and the iodide was immediately added, the error was eliminated. The results with 7 molal hydrochloric acid are consistent, but, owing to the large amounts of acid required, it is desirable to work at the lowest possible concentration. In Expt. 34 only half of the hydrochloric acid was added before adding the potassium iodide, making the hydrochloric acid slightly less than 6 molal during the vanadate–iodide reaction. The remainder of the acid was added when the titration was half finished.

Test Analyses: Effect of Presence of Other Constituents.—–In Table II are shown the results obtained when vanadium was present with various other substances. Here the final concentration of the hydrochloric acid was always approximately 6 molal. The amount of vanadium taken was 66.4 mg. in all cases (except in Expts. 6 and 9), and in every case 25 ml. of potassium iodide of the concentration shown in the table was used.

TABLE II

TITRATION OF VANADIUM WITH IODATE IN THE PRESENCE OF OTHER SUBSTANCES

Expt.	Subs. present, mg.	Concn. of KI soln., mole/liter	KIO_3 used, ml.	Vanadium found, mg.
1	7350 H_3PO_4 (75 millimoles)	0.05414	14.06	66.30
2	1000 Fe (as $FeCl_3$)	.05404	14.12	65.74
3	500 Fe	.05404	14.13	65.68
4	100 Fe	.05404	14.09	65.90
5	50 Fe	.05404	14.08	65.95
6	40 Fe[a]	.05414	21.89	26.41
7	1030 Fe, 75 millimoles of H_3PO_4	.05414	14.11	66.06
8	220 As (as As_2O_5)	.05414	14.08	66.21
9	266 As''	,05404	21.80	26.61
10	300 W,[b] 75 millimoles of H_3PO_4	.05414	14.11	66.06
11	1000 W,[c] 75 millimoles of H_3PO_4	.05414	14.12	66.01

[a] 26.58 mg. of vanadium taken.

[b] WO_3 was dissolved in the H_3PO_4.

[c] WO_3 was partly dissolved in the H_3PO_4.

Experiments 1, 6, 10 and 11 in Table II show that even a large excess of phosphoric acid has very little effect on the determination. This shows that any phosphate–vanadate complex molecule that is formed is not so stable as to prevent reduction of the vanadate. The presence of ferric ion, even in very large quantities, seems to cause only a slight, though apparently definite, decrease in the amount of vanadium found. The reason for this is not clear. The ferric chloride used was proved to contain no appreciable quantity of ferrous salt; moreover, the work of Heisig[3] shows the tendency of ferrous chloride solutions to oxidize rapidly in the presence of air under the conditions of this procedure; this would cause an effect opposite to that observed. Expts. 8 and 9 show that although arsenic acid oxidizes iodide, it is re-oxidized by iodine monochloride when titrated with iodate and does not interfere with this determination of vanadium. Expts. 10 and 11 show that tungstic acid can be held in solution with phosphoric acid and the titration made in its presence.

Final Analytical Procedure.—Upon the basis of the above experiments the following procedure is suggested. Bring the vanadium as vanadate into as small a volume of solution as possible, preferably not over 25 ml., in order to avoid the use of an excessive quantity of hydrochloric acid. Transfer the solution to a 200–400-ml. conical flask with a ground-glass stopper and pass for two to three minutes a rapid current of carbon dioxide into the flask, but not through the solution. Gently swirl the solution in the flask during this time. Add through a funnel to the solution in the flask such a volume of 12 molal hydrochloric acid as will make the solution 6–8 molal in acid during the vanadate–iodide reaction. Cool the flask with tap water during the addition of the acid. Add to the solution from a pipet or buret an excess (as small as practicable) of standard potassium iodide solution. Mix the solutions, let the flask stand for one to two minutes, add to it 5 ml. of carbon tetrachloride and then titrate with standard iodate solution, adding 12 molal hydrochloric acid as needed so that its concentration may never fall below 6 molal in the solution being titrated. Where the approximate amount of vanadium present is known, the calculated volume of hydrochloric acid can be added before the titration. When approaching the end-point shake the solution vigorously so that equilibrium of the iodine between the carbon tetrachloride and water layers is attained. Cool the solution with tap water during this shaking to prevent drops of the solution from blowing out around the stopper when the flask is opened.

As a direct test of this procedure some ammonium metavanadate from the same source as that used in preparing the vanadate solution was recrystallized, then ignited to the oxide at 400–500°. This product was moistened with nitric acid and again heated at the same temperature. Of this 1.4174 g. was weighed out, dissolved in sodium carbonate solution, the solution diluted to 100 ml., four 10-ml. portions were pipetted out and treated by the above procedure. The results obtained are shown below. The iodide solution was 0.05404 molal.

TABLE III

TEST ANALYSES FOR FINAL PROCEDURE

No.	1	2	3	4
Iodine added, ml.	35	35	35	35
Iodate used, ml.	22.25	22.27	38.47	38.50
Vanadium found, mg.	79.40	79.29	79.34	79.19

The calculated weight of vanadium present was 79.41 milligrams.

In No. 1 half of the hydrochloric acid was added before adding the potassium iodide and the remainder during the titration. In No. 2 all of the acid was added before the iodide, while in Nos. 3 and 4 half of the acid was added before the iodide and half just before beginning the titration.

Summary

A method for the volumetric determination of vanadium by means of standard solutions of potassium iodide and potassium iodate has been developed. The method depends upon the reduction of vanadate by a known amount of iodide in hydrochloric acid solution and conversion of the iodine formed and of the excess of iodide into iodine monochloride by titration with iodate.

It is shown that when the concentration of the hydrochloric acid is 6 molal or more, quadrivalent vanadium is not oxidized by the iodine monochloride and the reactions are quantitative.

Tests analyses proved that vanadate can be determined by this method in the presence of phosphate, arsenate or ferric iron, and also in the presence of tungstic acid, which may be held in solution by adding phosphoric acid.

PASADENA, CALIFORNIA

THE ABSORPTION SPECTRUM AND DECOMPOSITION OF HYDROGEN PEROXIDE BY LIGHT

BY H. C. UREY, L. H. DAWSEY AND F. O. RICE

RECEIVED NOVEMBER 28, 1928 PUBLISHED MAY 6, 1929

Very extensive studies have been made on hydrogen peroxide in dilute and concentrated solutions and recently in the pure liquid state.[1] These studies have dealt particularly with its thermal, photochemical and catalytic decomposition in solution.[2] No work has been done on its decomposition in the gaseous state other than that of Elder and Rideal,[3] showing that the thermal decomposition is predominantly a surface reaction.

---

[1] (a) Maass and Hatcher, THIS JOURNAL, 42,2548 (1920); (b) Maass and Hiebert, *ibid.*, 46,2693 (1924).

[2] For a complete review of this work, see Kistiakowsky, "Photochemical Processes," McGraw-Hill Book Co., Inc., New York, 1928, pp. 173–177.

[3] Elder and Rideal, *Trans. Faraday Soc.*, 23,545 (1927).

The thermal, photochemical and catalytic decomposition is undoubtedly a very complicated one and in view of the work of Rice and Reiff[4] and of Rice and Kilpatrick[5] on the effect of ultramicroscopic particles on the thermal and photochemical decomposition it seems that much of the previous work cannot be regarded as conclusive.

The absorption spectrum of hydrogen peroxide solutions has been photographed by Henri and Wurmser,[6] who found that it was continuous, but no studies have been made on its absorption spectrum in the gaseous state and no determinations of the coefficient of absorption at different wave lengths, either in solution or as a gas. It was the purpose of this research to investigate these two subjects to see what light they might throw on the photochemical decomposition.

Preparation of the Hydrogen Peroxide.—We have used the methods of Maass and Hatcher[1] and of Rice, Reiff and Kilpatrick[7] in the preparation of the hydrogen peroxide. For the study of the dilute solutions, a 30% solution of the trade substance, Superoxol, was diluted down to the required concentration and in order to get more concentrated solution the water was evaporated off in a vacuum desiccator over sulfuric acid to a concentration of 88 to 90%. From this point pure hydrogen peroxide was made by repeated crystallizations. The strength of the hydrogen peroxide was determined by titration with potassium permanganate, The concentration of the liquid used in the study of light absorption of the vapor was always greater than 95%.

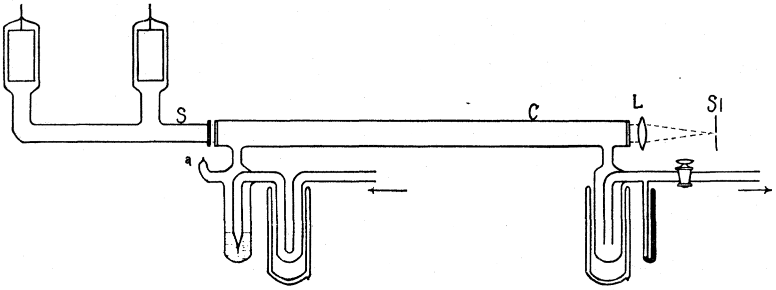


Fig. 1.

Apparatus for Determining the Absorption Spectrum.—In Fig. 1 is given a sketch of the apparatus, which remained essentially the same throughout the various experiments on absorption, though different types of absorption cells were used at different times. A hydrogen vacuum discharge tube, similar to that used by Tingey and Gerke[8] in their study of the absorption spectra of the hydrogen halides, was used as a source of continuous light and is shown in the figure at S. Electrolytic hydrogen was sealed off into the pyrex tube after degassing by passing a strong discharge through the tube, which raised it to a temperature of about 300°. A quartz window was sealed to the end with de Khotinsky cement to allow the passage of the ultraviolet light. We found

---

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

[5] Rice and Kilpatrick, *ibid.*, **31**, 1507 (1927).

[6] Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913); *ibid.*, **157**, 126, 284 (1913).

[7] Rice, Reiff and M. L. Kilpatrick, THIS JOURNAL, **48**, 3019 (1926).

[8] Tingey and Gerke, *ibid.*, **48**, 1838 (1926).

that at the high pressures of hydrogen within the tube necessary for the production of the hydrogen continuous (about 3 mm. of mercury) it was not satisfactory to cool the tube, with water directly, due to puncture of the glass by the high potential required to produce the discharge but we had to immerse it in transformer oil through which water circulated in a copper coil. The tube gave a dense continuous emission extending from the sensitivity of our plates in the green down inta the Schumann region. The maximum of the intensity of the continuous emission appeared to be about 3500 Å., though due to the greater dispersion in the ultraviolet is undoubtedly further to the violet. The first three lines of the Balmer series appeared; the green line was intense, and **the** blue line weak, being lost in the continuous. The color of the discharge was light blue with a tinge of pink. The current was supplied to the tube from a separate 110-volt, 60-cycle generator and stepped up to about 5000 volts across the tube. The current in the primary of the transformer was kept at 25 amperes and thus the emission intensity of the discharge tube remained quite constant. This tube has been used through the course of a year without renewing the hydrogen. The light from this source was passed through the absorption cell, C, of which several kinds were used. The light passing through the cell is approximately parallel due to the fact that the light from the luminous portion of the discharge tube passed through about 10 cm. of tubing before passing the quartz window. **A** lense at **I**, focused the light on the slit of the spectrograph at S1.

Two Hilger quartz spectrographs were used in our measurements, the larger, E-3, being used for the absorption curve, and the small one, E-37, to investigate the region 1850 to 2350 Å. and the fluorescence. **A** Hilger rotating sector photometer was used to vary the times of exposure in the comparison photometry to estimate the coefficient of absorption.

In the first experiment a quartz cell was constructed of 67.5 cm. length and **3** cm. diameter, and it was so arranged that the temperature of the cell and containing bulb could be raised to any desired temperature between 25 and 100° by means of an electrical heating coil surrounding both cell and containing bulb. The absorption spectrum of the vapor photographed through this cell held at different temperatures showed that the spectrum is continuous throughout the range from 2000 to **3100** Å. No absorption could be detected on our plates for wave lengths longer than about 3000 or 3100 Å., but the absorption extends further to the violet with no indication of a maximum in this region. It was impossible to duplicate the intensities of blackening for the same wave length in different experiments at temperatures above 25°, probably due to poor temperature control and thermal decomposition of the vapor. For this reason experiments at higher than room temperature were discontinued.

By using a cell 183.5 cm. in length and **3** cm. in diameter, it was possible to get the product of concentration and the length sufficiently great to determine the coefficient of absorption at 2750 **Å.** and shorter wave lengths with a vapor pressure of about 1.5 mm., corresponding to 20°. This long cell was constructed of a pyrex tube with quartz windows sealed on with de Khotinsky cement. The hydrogen peroxide vapor at room temperatures did not attack the de Khotinsky cement appreciably, though such action is to be expected. No difference in the absorption could be detected when this cell was used and when other shorter cells not having the de Khotinsky cement were used.

Method for Determining the Coefficient of Absorption.—The coefficient of absorption per molecule is defined by the formula

$$I = I_0 e^{-acd} \text{ or } a = 1/cd \ln I/I_0 \qquad (1)$$

where c is the concentration in molecules per cc., d the length of the column of gas and I and I_0 are the intensities after passing through the filled and empty cells, respectively. Assuming that

$$I/I_0 = t_0/t \tag{2}$$

where t_0 and t are the times required for the plate to be blackened to the same extent at a particular wave length by the light passing through the empty cell and the filled cell, respectively, we have

$$a = 1/cd \ln t_0/t \tag{3}$$

In our experiments it was necessary to use rather wide absorption cells because of the great length of absorbing vapor at low pressures required to secure absorption and this made it impossible to use two parallel identical cells, one empty and the other filled, as is usually done. We therefore adopted the following procedure. Exposures of the continuous spectrum through the empty cell for different values of $\ln t_0$ were taken, leaving alternate spaces on the photographic plate unexposed; then with the cell filled with the absorbing vapor exposures were made at these intermediate positions, using different values of $\ln t$. In this way we cannot compare the intensities of two spectra lying right side by side. We therefore matched the limit of the observable blackening of the plate. Taking two spectra, one through the empty cell and one through the filled cell having the same limit of blackening, the coefficient of absorption for this wave length is secured by substituting the values of $\ln t$ and $\ln t_0$ for these two spectra in (3) and it was found by trial that this limit was very reproducible. This method differs from the more usual one only in that we match the blackening on the plate for the point of zero blackening instead of at a finite intensity of blackening. We believe the errors of observation by this method are at least not much greater than in the more usual method.[10] Variation in the intensity of illumination was avoided by maintaining the current in the primary of the transformer constant during the experiments. We believe that this variation is small even over several hours, since the tube has been in use for months and therefore should not change with time, and, since it is well cooled, there should be no variation due to temperature. In practice we found it best to plot curves of $\ln t$ and $\ln t_0$ against wave length for the limits of blackening for the light passing through the filled cell and empty cell, respectively, and take the difference in $\ln t$ and $\ln t_0$ for a particular wave length from these curves.

Method of Experimental Procedure.—Into the bulb, a, a quantity of 97–100% hydrogen peroxide was introduced and air was bubbled through the liquid after first passing through the U-tube cooled in liquid air to remove all moisture. The dry air was admitted through a capillary tube and bubbled slowly through the liquid hydrogen peroxide to insure saturation with the vapor at the temperature of the bulb. Thus a constant current of vapor at a constant partial pressure streamed through the absorption cell while the absorption was being measured. This method of distilling the vapor partly eliminated the decomposition effect of the hydrogen peroxide due to the ultraviolet light. The total pressure maintained during a measurement was about 300 mm. of air and hydrogen peroxide. The hydrogen peroxide and any water produced were caught at the right end of the absorption cell in another liquid-air trap, beyond which were the mercury manometer and the oil pump.

---

[9] Schwarzschild first wrote this equation in the form $I/I_0 = (t_0/t)^n$ where n is slightly less than unity. Recent work by Gibson, McNicolas, Tyndall and Frehafer (Scientific Papers of the Bureau of Standards, No. 440, June, 1922) and by Baly, Morton and Riding, Proc. Roy. *Soc.* London, **113A**, 709 (1927), shows, however, that the exponent may be taken as unity with an error of not over a few per cent.

[10] Henri, "Études de Photochimie," Gauthier-Villars et Cie, Paris, 1919.

The bulb was held at a temperature of about 20° so that the vapor pressure according to Maass and Hatcher[10] is 1.5 mm. The value of *cd* is therefore $cd = 2.702 \times 10^{19} \times 273/293 \times 1.5/760 \times 183.5 = 0.88 \times 10^{20}$. We believe that this value is correct within about 10 to 20%. The possible sources of error are the rapid change of the vapor pressure with temperature, the incomplete saturation of the air passing through the liquid and any decomposition of the hydrogen peroxide due to the light and hear.

The coefficients of absorption of the aqueous solutions were determined by using a cell 5 cm. in length and varying the concentration in order to get suitable blackening at different wave lengths. Absorption begins between 3700 and 3800 Å.; the absorption coefficient increases slightly to 3000 Å., after which it increases rapidly with decreasing wave length. These *cd* values were correct to within 1 or 2% because of the more precise method for determining the concentration.

Table I is a summary of our measurements and Pig. 2 shows them in graphical form. The circles represent values of a calculated from two plates for the solution and show the magnitude of deviation from the mean value. The crosses represent the absorption coefficients for the vapor. These cannot be regarded as very precise because of the uncertainty of the cd, but within this estimated uncertainty the curves for the vapor and solution coincide.

TABLE I

SUMMARY OF MEASUREMENTS

Wave length	Mean a	Number of plates	Wave length	Mean a	Number of plates
3800	0	2	2700	4.1	6
3700	0.1	2	2650	5.4	7
3600	0.2	2	2600	6.9	7
3500	0.2	2	2550	8.3	4
3400	0.3	2	2500	10.2	4
3300	0.4	2	2450	12.2	3
3200	0.5	3	2400	14.7	3
3100	0.7	3	2350	17.9	3
3000	1.0	4	2300	22.0	3
2900	1.5	5	2250	25.6	3
2800	2.4	5	2200	28.9	3
2750	3.1	5	2150	31.5	3

Value of *cd* for the vapor $= 0.882 \times 10^{20}$; values for the liquid $cd = 1.148, 0.579, 0.289, 0.114, 0.0723, 0.0362 \times 10^{20}$.

Discussion of the Absorption Experiments.—Since the spectrum is continuous, with no structure of any kind, we must conclude that the elementary process of the absorption of light is to dissociate the molecule into two or more fragments in accordance with Franck's[11] interpretation of continuous absorption spectra of the hydrogen halides and halogens. The conservation of energy requires that the energy of the quantum absorbed shall be

$$h\nu = E_1' + E_2' + \ldots\ldots + D + {}^1/_2M_1v_1^2 + {}^1/_2M_2v_2^2\ldots\ldots \qquad (4_2)$$

---

[11] For the theory of the dissociation process see Franck, *Trans. Faraday Soc.*, 21, 536 (1925); Condon, *Phys. Rev.*, 28,1182 (1926).

where E'_1, E'_2...... are the energies of excitation of the resulting molecules, D is the energy of dissociation and $^1/_2M_1v_1^2$, $^1/_2M_2v_2^2$.... are the kinetic energies of the resulting molecules relative to the center of mass of the system. Since these resulting molecules can have unquantized kinetic energy of translation, the continuous absorption spectrum will lie on the violet side of the wave length for which

$$h\nu = E'_1 + E'_2 + \ldots\ldots + D \qquad (5_2)$$

and any discontinuous spectrum on the long wave length side. It may happen that the main intensity of absorption may occur considerably toward the violet side of this limit and thus only a continuous spectrum will be observed. This appears to be true of hydrogen peroxide. In the case of the alkali halides and hydrogen halides[12] only such continuous absorption spectra are observed, while in the case of the halogens the discontinuous and continuous absorption spectra are both known and meet at the frequency defined by (5). These considerations are repeated here because they have a direct bearing on the interpretation of this continuous spectrum.

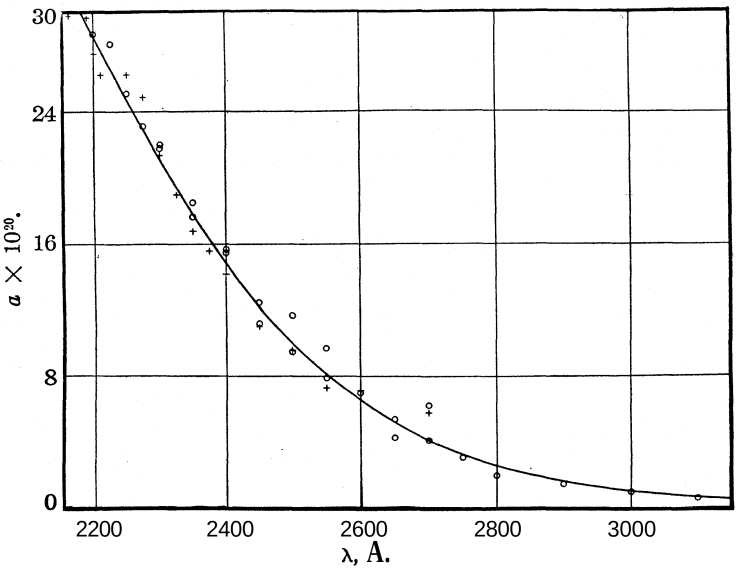


Fig. 2.

Henri has found that such continuous spectra are observed for associated vapors and there is a possibility that the absorption in the vapor state is due to the presence of a small percentage of $(H_2O_2)_n$. The absorption of light by such a molecule might result in its dissociation into

---

[12] Franck, Kuhn and Rollefson, *Z. Physik*, 43, 155 (1927); Franck and Kuhn, *ibid.*, 43, 164 (1927); 44, 607 (1927); Franck and Hogness, *ibid.*, 44, 26 (1927).

one excited and one unexcited molecule and thus even if the molecule is not dissociated into atoms or unstable molecules such as OH, the spectrum might be continuous. Most of our work has been done at very low pressures, however, and under these conditions we expect that any such association would be very small. Elder and Rideal[3] find no evidence of association of hydrogen peroxide at 85 mm. and 85°. Kendall[13] has considered the question of association of water vapor and concludes that over a considerable range of pressures and temperatures there is no evidence for association. Because of the great similarity of physical properties of hydrogen peroxide and water, this makes it probable that such association of hydrogen peroxide must be small. Even if a continuous absorption of a very small fraction of polymerized molecules were present, one would expect a band spectrum of greater intensity superimposed on it. The absence of such a band spectrum indicates that the normal unassociated molecule must also have a continuous absorption spectrum. The question could be definitely decided by studying the absorption of the vapor at high and low pressures with the same value of cd, for the absorption should be greater at the higher pressures if polymerized molecules are responsible for the absorption and it should be the same if the unpolymerized molecules are responsible for the absorption. This would be very difficult with hydrogen peroxide because of its low vapor pressure at temperatures where thermal dissociation is slow. Thus to compare the absorption by two columns of vapor, one at 1.5 mm. pressure and say 183 cm. long, and another at 0.15 mm. pressure and some 18 meters long, would be impossible.

Hydrogen peroxide may be considered to be a pseudo-halogen. The normal states of the halogen atoms are inverted ^2P states with inner quantum numbers 3/2 and 1/2, the 3/2 state being the one with lower energy. Similarly, the OH molecule has the same number of electrons as the fluorine atom and also its normal state is an inverted ^2P state according to Mulliken.[14] We may make the postulate that the hydrogen peroxide molecule is formed of two OH molecules in a way similar to the formation of the halogen molecules from the individual atoms. Our experiments on the absorption of light described above support such an assumption. It is true, of course, that in chemical and physical properties there is very little similarity between hydrogen peroxide and the halogens, but the curves for the coefficients of absorption for I_2, Br_2 and Cl_2 show a progressive change which would lead us to expect that this curve for hydrogen peroxide would lie as it does. According to Ribaud and Kuhn,[15] the maxima for the absorption by I_2, Br_2 and Cl_2 lie 400,

---

[13] Kendall, THIS JOURNAL, 42, 2477 (1920).

[14] Mulliken, *Phys. Rev.*, N. S., 32, 388 (1928).

[15] Ribaud, *Ann. Physik*, 12, 107 (1919); Kuhn, *Z. Physik*, **39**, 77 (1926).

900 and 1400 Å., respectively, to the violet side of the critical wave lengths required for dissociation into a normal and excited atom, respectively. These critical wave lengths are 4995, 5107 and 4785 Å. and thus the three maxima lie at 4595, 4207 and 3385 Å., respectively. The absorption spectrum of fluorine is unknown, but it would probably have a maximum absorption at a considerably shorter wave length than that of chlorine, and if the action of light on the hydrogen peroxide molecule is similar, the maximum should also lie to the violet side of that for chlorine, as it does. The continuous absorption by I_2, Br_2 and Cl_2 is due to molecules in the lowest vibrational state; in the case of Cl_2 absorption by molecules in the lowest vibrational state occurs only in the continuous region, and its band spectrum is due to absorption by molecules in the first or second vibrational state. In the case of hydrogen peroxide it appears that molecules in all the vibrational states present in appreciable number at 20° absorb only in the continuous region, and that this continuous region is far to the violet side of the critical wave length for dissociation. We shall now consider in detail the known energy relations for the various conceivable ways that the molecule could dissociate.

Assuming hydrogen peroxide to have the structural formula H–O–O–H, it appears that primary dissociation might occur in three ways, namely, to produce two OH molecules in their normal states, or to break off one H atom leaving the HOO molecule; the removal of an oxygen atom from the middle of the molecule, thus leaving a water molecule, appears less probable. We wish to calculate the energy change for these three reactions from known data. In the thermochemical equations which follow, we employ the usual convention in regard to sign of the energy change, namely, the energy of the products minus that of the reactants. The energy of dissociation into H_2O and O can be exactly calculated as follows

$$\begin{array}{lll}
\text{(a)} & \mathrm{HOOH = HOH + {}^1/_2O_2} & -25.2\ \text{cal.}^{16} \\
\text{(b)} & \mathrm{{}^1/_2O_2 \;\;= O} & 81.0\ \text{cal.}^{17} \\
\hline
\textit{(c)} & \mathrm{HOOH = HOH + O} & 55.8\ \text{cal.}
\end{array}$$

The energy change for dissociation into two OH molecules cannot be exactly calculated, but can be approximated from the following equations

$$\begin{array}{lll}
\text{(a)} & \mathrm{HOOH = HOH + {}^1/_2O_2} & -25.2\ \text{cal.} \\
\text{(d)} & \mathrm{2HOH = 2H + 2OH} & 224.0\ \text{cal.}^{18} \\
\text{(e)} & \mathrm{2H \;+ = He} & -102\ \text{cal.}^{19} \\
\text{(f)} & \mathrm{H_2O + {}^1/_2O_2 = HOH} & -57.8\ \text{cal.}^{16} \\
\hline
\text{(g)} & \mathrm{HOOH = 2OH} & 39\ \text{cal.}
\end{array}$$

---

[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 477 and 495.

[17] Birge and Sponer, *Phys. Rev.*, N. S., 28,259 (1926).

[18] Taylor and Bates, *Proc. Nat. Acad. Sci.*, 12, 714 (1926); THIS JOURNAL, 49, 2438 (1927).

[19] Witmer, *Phys. Rev.*, 28, 1223 (1926); Dieke and Hopfield, *Z. Physik*, 40, 299 (1926).

The uncertainty in this figure is in the energy required to remove one hydrogen atom from water and this is less than 112 cal., since Taylor and Bates were able to dissociate water vapor with mercury atoms excited to the $^3P_1$ state. The energy change for dissociation into HOO and H cannot be calculated. The energy change for the reaction $HOOH = 2H + O_2$ can be calculated from the following equations

(h) $HOOH = H_2 + O_2$ 32.6 cal.[16]
(e) $H_2 = 2H$ 102.0 cal.[19]

(i) $HOOH = 2H + O_2$ 134.6 cal.

and assuming that the change for the removal of the two hydrogen atoms, successively, is the same, we have

(j) $HOOH = HOO + H$ 67.3 cal.
(k) $HOO = H + O_2$ 67.3 cal.

In the case of water the removal of the first hydrogen requires less energy than the second, for from the equations given for the dissociation of O_2 and H_2 and the energy of formation of water, (b), (e) and (f), we have

(m) $HOH = 2H + O$ 240.8 cal.

and thus using (d)

(n) $OH = O + H$ 128.8 cal.

From analogy, the energy change for (j) may be less than 67.3 cal. and that for (k) greater than 67.3 cal., though this is not necessarily true.

The longer wave-length limit of absorption of the liquid is about 3750 Å., which is equivalent to 76.2 cal., and the longest wave length for the observed absorption of the vapor is about 3000 Å., corresponding to 95 cal. Over the range from 2250 to 2750 Å., where we found it possible to determine the coefficients of absorption for the solution and the gas, these coefficients agree within the limits of our measurements. It was impossible to determine the absorption coefficient for the gas at longer wave lengths because of the impossibility of getting a larger value of *cd* without increasing the temperature. It may be that the vapor would also absorb out to 3750 Å., if a sufficiently thick layer could be secured. It is evident in any case that there is sufficient energy even at 3750 Å. to cause any of the three reactions postulated to take place, and give considerable kinetic energy of translation or internal vibrational or rotational energy to the products. We cannot on this basis alone exclude any of them.

Effect of an Electric Discharge on Hydrogen Peroxide.—It is well known that the so-called water bands due to the OH molecule and the atomic spectrum of hydrogen appear with great intensity when water vapor is excited by an electric discharge at low pressures. The atomic oxygen spectrum appears only with comparatively low intensity. With a condensed discharge, or, if the discharge tube is allowed to become hot, the oxygen spectrum appears. We interpret this to mean that the comparatively low velocity electrons of the uncondensed discharge cause a disruption of water molecules into excited or unexcited OH molecules and H-atoms. The faintness of the O and H_2 spectra indicates that these are not primary products of bombardment of water in the uncondensed discharge.

An uncondensed electric discharge in hydrogen peroxide gives quite a different spectrum from that of water, if the hydrogen peroxide is streamed rapidly through the discharge tube, and the tube is kept well cooled. In these experiments hydrogen peroxide of nearly 100% purity was passed through a quartz tube 1 cm. in diameter by evaporating liquid hydrogen peroxide from a side arm of the tube and condensing it and any water formed in a liquid-air trap and pumping off the gases. Under these conditions the hydrogen peroxide must have been in this discharge only 0.1 to 0.01 second. As long as the tube was cool and the evaporation of hydrogen peroxide was rapid, the tube had a dull blue color in contrast to the characteristic red color of the discharge in water. By using a spectroscope we found that both atomic and molecular spectra of hydrogen were almost entirely absent. The faint blue color of the tube is due to a faint continuous spectrum. A photograph of the spectrum with the quartz spectrograph shows that the water bands are very intense and also that the continuous in the ultraviolet is faint. We are unable as yet to decide whether the continuous spectrum is identical with that of hydrogen or not.

The absence of the molecular and atomic spectra of hydrogen under these conditions leads us to believe that the comparatively slow electron bombardment causes the dissociation of hydrogen peroxide into two normal OH molecules and their subsequent excitation, or into one excited and one unexcited OH molecule, or into two excited OH molecules, so that the predominant spectrum is that of the water bands. The dissociation in such a way that oxygen or hydrogen atoms appear is at least much less probable. Since inelastic collisions of electrons with atoms and molecules are more probable, if the transition is one permitted by the selection rules for the emission and absorption of light, this experiment favors the postulate that light also dissociates hydrogen peroxide into normal or excited OH molecules.[20]

Experiments on the Fluorescence of Hydrogen Peroxide.—Our calculations on the energy changes thus far have considered only the dissociation into molecules in their lowest energy states. If the dissociation of hydrogen peroxide by light is similar to that of the halogens, the one OH molecule should be left in a $^2P_{1/2}$ state and the other in a $^2P_{3/2}$ state. However, since the energy difference of these two states is only 140.25 wave numbers according to Kemble,[21] which is equivalent to only 0.4 cal., and of the

---

[20] See Franck and Jordan, "Handbuch der Physik," Julius Springer, 1926, Vol. 23, p. 721.

[21] Kemble, Phys. *Rev.*, N. S. 30,387 (1927).

order of the rotation energy of the molecule, it is too small to be of importance in our thermochemical calculations. The next higher state is probably the ^2S state, which is the excited state for the emission of the water bands. Five of these bands are well known; their wave lengths and the initial and final values of the vibration quantums, n', and n'', are: 3064 (0,0); 2811, (1,0); 2875 (2,1); 2608 (2,0); and 3428 (0,1).[22] The wave numbers of the 3064, 2811 and 2608 bands give directly the energies required to excite the OH molecule to the ^2S state with vibrational quantum numbers 0, 1 and 2, respectively. These wave numbers are 32,637, 35,575 and 38,343, respectively. If then hydrogen peroxide is illuminated with light of sufficiently high wave number to dissociate the molecule into a normal OH molecule and an excited OH molecule in a ^2S state and one of these vibrational states, and if the dissociation in this way is a possible one, it should be possible to observe the OH bands in fluorescence under proper conditions. The essential experimental requirements are *intense illumination of the vapor at low pressure* so that the fluorescence is not quenched by collisions with other hydrogen peroxide molecules or water molecules. Since the vapor pressure of water at 20° is 17.4 mm. of mercury, while that of hydrogen peroxide is only 1.5 mm., it is necessary to use very pure hydrogen peroxide.

The energy required to dissociate hydrogen peroxide into two normal OH molecules is less than 39 cal. (Eq. g), which is equivalent to 13,660 wave numbers. The wave number, $\tilde{\nu}$, and wave lengths of the light required to dissociate the molecule and excite the one OH molecule to the ^2S state with different amounts of vibrational energy are

		$\tilde{\nu}$	λ
(g)	$HOOH = \mathrm{OH}(^2P) + \mathrm{OH}(^2P)$	13660 cm.$^{-1}$	7320 Å.
(o)	$HOOH = \mathrm{OH}(^2P) + \mathrm{OH}(^2S, n' = 0)$	46350 cm.$^{-1}$	2160 Å.
(p)	$HOOH = \mathrm{OH}(^2P) + \mathrm{OH}(^2S, n' = 1)$	49020 cm.$^{-1}$	2040 Å.
(q)	$HOOH = \mathrm{OH}(^2P) + \mathrm{OH}(^2S, n' = 2)$	52050 cm.$^{-1}$	1920 Å.

Hydrogen peroxide vapor at a pressure of about 1 mm. of mercury was illuminated with the 2025, 2060, 2087, 2100 and 2138 Å. lines of the zinc spark, and the presence of the 3064 Å. water band was detected in fluorescence. The light from a zinc spark was passed through an acetone filter, which absorbed all the light from 2138 to 3075 Å., and transmitted longer wave lengths and shorter wave lengths to about 2025 Å., so that this zinc line is faint. The longer wave lengths are only slightly absorbed by hydrogen peroxide and are therefore of no importance. The zinc

---

[22] For references see Mulliken, *Phys. Rev.*, 32, *403 (1928)*; L. Grebe and *O.* Holtz, *Ann. Physik*, 39, *1243 (1912)*; T. Heurlinger, "Dissertation," Lund, 1918; R. Fortrat J. *Phys.*, 5, *20 (1924)*; W. *W.* Watson, *Astrophys.* **J.**, 60, *145 (1924)*; *G. H.* Dieke, *Proc. Acad. Sci. Amsterdam*, 28, *174 (1925)*; *R. T.* Birge, Chapter LV, Part **5**, National Research Council Report on Molecular Spectra in Gases; D. Jack, *Proc. Roy. Soc. London*, **115A**, *373 (1927)*; **118A**, *647 (1928)*; *E.* C. Kemble, *Phys. Rev.*, 30,337 *(1927)*.

spark has only the five strong lines between 2138 Å. and 2025 Å. Thus these five intense lines and less intense ones are the only ones effective in producing fluorescence. After passing the acetone filter the light passed through a long cell of hydrogen peroxide vapor. The spectrograph was placed in the direct line of this incident light. The photographic plate showed these incident wave lengths strongly so that the entire tube must have been excited to fluorescence. The fluorescent water bands fall in the region of absorption of acetone so that the presence of the incident light on the plate did not prevent the detection of the fluorescent light. The head of the 3064 Å. water band falls about 11 Å. to the short wave-length side of the 3075 Å. line of the zinc spark and appears as a faint sharp edge just in this position. No other water bands were detected, probably because of their lower intensities or because the light used may not be of sufficiently short wave length to excite the higher vibration levels.

This experiment shows definitely that the reaction (o) is one possible way in which light dissociates the molecule.[23]

One of us (L. H. D.) is continuing this phase of the work with better methods for exciting this fluorescence expecting to secure the other water bands and determine, if possible, the energy change of (g) more accurately by this method. Furthermore, the recent work of Kondratjew and Leipunsky[24] on the recombination spectra of the halogens and that of Bates and Urey[25] on the continuous spectra emitted by flames containing hydrogen and the halogens and interpreted by them as the recombination spectra of halogen atoms, suggest that further study of the continuous emission spectrum of hydrogen peroxide may give more information

---

[23] Since the writing of this paper an article has appeared [Bonhoeffer and Haber, *Z. physik. Chem.*, 137, **263 (1928)**] in which the heat of dissociation of the OH molecule has been taken as **123** cal. and the energy of dissociation of the first H atom from the water molecule as **115** cal. The energy of dissociation of hydrogen peroxide into gaseous hydrogen and oxygen is taken as **38** cal. by a different method of calculation. However, the value of **32.8** cal. for the energy of formation of hydrogen peroxide as calculated by Lewis and Randall[16] seems to us a better value than that calculated by Wartenberg and Sieg [*Ber.*, 53, **2192** (1920)] and the energy of formation of water from the atoms is **240.8** according to our calculations. These values have not been calculated to absolute zero and are therefore not very accurate. If the value of 54 Cal. for Equation (g) is correct, we should not have been able to secure the **3064 Å.** water band in fluorescence and in fact the energy change in this reaction cannot be much greater than **39** cal. if the **3064** Å. band is to be excited by the wave lengths we have used. The photochemical experiments of Bates and Taylor[18] and Senftleben and Rehren [Z. *Physik*, 37, **529** (1926)] and also Bonhoeffer and Reichardt [Z. *Elektrochem.*, 34, **652** (1928)] on the equilibrium $2H_2O = H_2 + 2OH$ at high temperatures indicate that **115** cal. is too large. If we use **115** cal. instead of **112** cal. and leave the remaining values in our calculations the same, the water band should not appear in our experiments.

[24] Kondratjew and Leipunsky, *Z. Physik*, 50, **366 (1928).**

[25] Bates and Urey, *Phys. Rev.*, N. S., article to appear soon.

in regard to the processes taking place in the discharge; this will be studied further.

Summary

1. The absorption spectrum of hydrogen peroxide vapor in the ultra-violet has been found to be continuous with no indication of any structure beginning at about 3000–3100 Å. and extended toward the ultra-violet.

2. The coefficients of absorption of hydrogen peroxide in solution have been determined for wave lengths from 3750 to 2150 Å. and those of its vapor for wave lengths 2150 to 2750 Å. Over this latter range and within the limits of experimental error the two absorption curves are the same.

3. The possible photochemical processes are discussed and it is found that the quantum of energy of the longest wave lengths absorbed would be more than sufficient to cause any of the following three reactions to take place

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad H_2O_2 + h\nu \longrightarrow HO_2 \qquad H_2O_2 + h\nu \longrightarrow H_2O + O$$

4. The emission spectrum of hydrogen peroxide when streamed rapidly through a cool discharge tube is predominantly that of the water bands (due to OH). This favors the first of these three reactions as the one occurring in the photochemical process.

5. Illumination with the zinc spark lines from 2025 to 2138 Å. caused the water bands to appear in fluorescence. This shows that the following reaction takes place under these conditions

$$H_2O_2 + h\nu = OH(^2P) + OH(^2S)$$

6. The analogy of hydrogen peroxide to the halogens with respect to structure is pointed out and the evidence, though not conclusive, favors the following reaction as the one occurring when it is illuminated with wave lengths from about 2200 to 3000 Å.

$$H_2O_2 + h\nu = OH(^2P_{1/2}) + OH(^2P_{3/2})$$

This would be similar to the primary process occurring when the halogens absorb light in the continuous region of their spectra.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

THE NEAR INFRA-RED ABSORPTION SPECTRA OF SOME ALDEHYDES, KETONES, ESTERS AND ETHERS

BY JOSEPH W. ELLIS

RECEIVED DECEMBER 11, 1928 PUBLISHED MAY 6, 1929

The infra-red absorption spectra of a group of aldehydes, ketones and esters have been obtained in the wave length region shorter than 2.5 μ with the primary purpose of ascertaining whether there are any features in such spectra assignable to the carbonyl group. The spectra of ethyl sulfate, pentane and three ethers have also been recorded for comparison purposes. The technique adopted was similar to that followed in some previous investigations by the author.[1] A few changes in the procedure of securing these absorption records are perhaps worthy of mention.

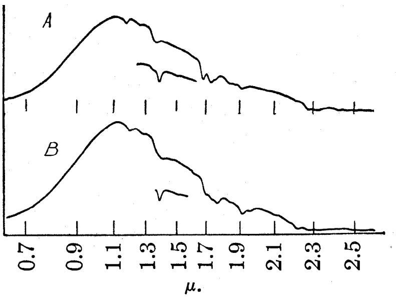


Fig. 1.—A, Acetaldehyde; B, propionaldehyde.

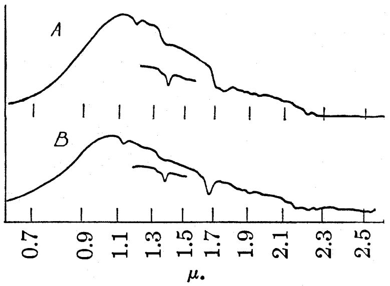


Fig. 2.—A, Butyraldehyde; B, benzaldehyde.

The tungsten lamp, rated at 7.5 amperes, was operated on much higher currents during this investigation. This permitted the use of narrower slits in the spectrograph. In obtaining the first set of records, Figs. 1–13, the initial slit and the one in front of the thermopile had a width of 0.152 mm. A slit of this width covers a spectral region of about 0.007 μ in the vicinity of 1.8 μ. The cell thickness, with two exceptions to be mentioned later, was 1 mm. The lamp source was operated on 9 amperes. The second set of records, Figs. 14–23, was for a cell thickness of 40 mm. The current was increased to 10 amperes and the slits narrowed to 0.127 mm., which is equivalent to about 0.006 μ at 1.8 μ.

With slits as narrow as this it was found impractical to adopt the previous method of using a visible emission spectrum line for a standard of reference. Consequently, it was decided to use the relatively sharp 1.39 μ absorption band of a 2-mm. cell of chloroform. To see whether it would be permissible to rack the plate-holder back to the vicinity of 1.4 μ

---

[1] (a) Ellis, THIS JOURNAL, 49,347 (1927); (b) 50,685 (1928).

after an absorption record had been taken, for the purpose of tracing the chloroform band, several records of absorption curves were retraced on their original plates. The almost exact superposition of these records indicated that it would be practicable to rely upon this method of superposing a standard baod upon the plate. This reference band is found in Figs. 1–13.

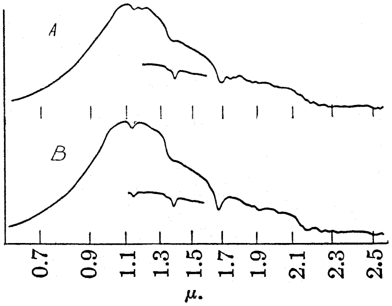


Fig. 3.—A, p-Tolualdehyde; B, cinnamaldehyde.

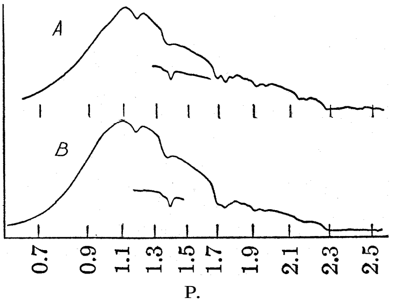


Fig. 4.—A, Acetone; B, methyl-n-propyl ketone.

It was discovered during the investigation, however, that there was an occasional record in which the 1.39 μ band was apparently shifted with respect to the spectrum recorded. This shift was ascertained from the following two observations. (1) As a result of a study of a considerable number of organic compounds, it becomes possible to predict fairly accurately the wave length positions of certain recurring bands. (2) A considerable increase in resolving power resulting from a narrowing of the slits revealed the identity of the so-called P, Q and R branches of the 1.87 μ atmospheric water-vapor band. The sharp Q branch is observable not only in the intensity distribution curve of Fig. 13A but also in all of the absorption records of Figs. 1–13. This band, therefore, was chosen as the reference line in these measurements. In obtaining the records of Figs. 14–23 the 40-mm. cell was removed near 1.5 μ although the record

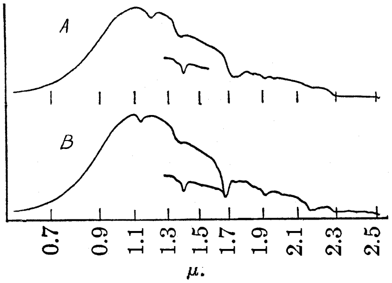


Fig. 5.—A, Methyl-n-amyl ketone; B, acetophenone.

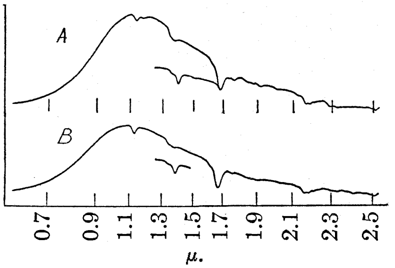


Fig. 6.—A, Propiophenone; B, benzophenone.

was continued to include the 1.87 μ water-vapor band. This reference band, however, has not been included in the figures.

Of the twenty-five compounds whose absorption curves are here presented eighteen contain a single carbonyl group, $=C=O$, while two others contain two such groups. Pentane and ethyl sulfate were included to show the behavior of a typical hydrocarbon and a typical alkyl radical, respectively. The three ethers were studied to see if any features appear which are characteristic of the oxygen atom in the chain.

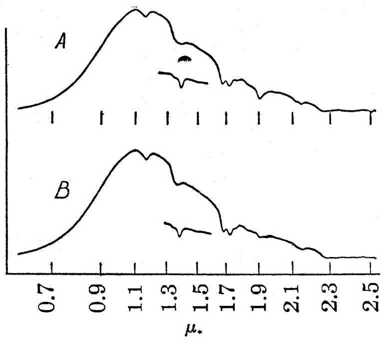


Fig. **7.—A,** Methyl acetate; B, ethyl acetate.

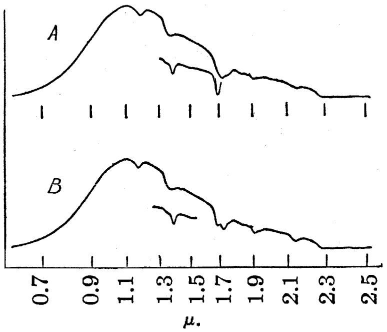


Fig. **8.—A,** ***n*-Butyl** acetate; B, ethyl **malonate.**

All of the compounds are liquids at room temperature except quinone and benzophenone, which are solids. These latter two substances were therefore examined in carbon tetrachloride solution. A 40-mm. cell of the solution containing an amount of the solid equivalent to a 1-mm. thickness of the material in its crystalline state was used. Their spectra have been included with the 1-mm. cell records of the liquid compounds. All of the materials whose absorption spectra are here presented were purchased from the Eastman Kodak Company.

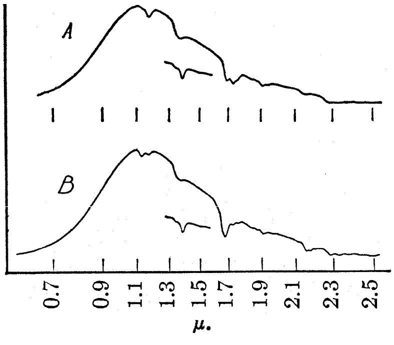


Fig. **9.—A,** Ethyl propionate; B, ethyl benzoate.

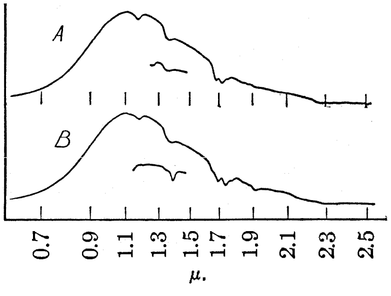


Fig. **10.—A,** Ethyl sulfate; B, acetylacetone.

Several investigations, mainly in the infra-red, already described in the literature, have some bearing upon the present study. Smith and Boord[2] in an investigation apparently undertaken to test the present author's previous conclusion that there is a C–H series of absorption bands characteristic of carbon–hydrogen compounds, included in their group of substances several of which contain the carbonyl group. Their investigation did not extend beyond 2.5 μ. The resolution of bands which they secured was good in spite of the fact that they used a spectroscope equipped with a single 60° rock-salt prism. The region covered by them was the same as that covered in this investigation. However, the quartz prisms used here gave a dispersion and a resolution many times that secured by Smith and Boord. This is shown by a comparison of absorption curves of the three substances common to both investigations.

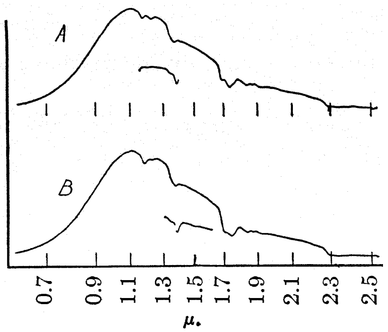


Fig. 11.—A, Ethyl ether; B, n-propyl ether.

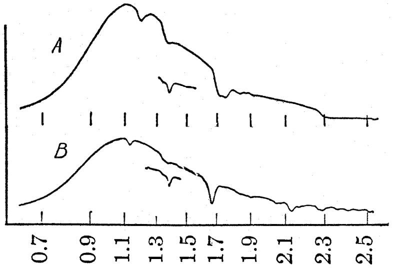


Fig. 12.—A, n-Butyl ether; B, quinone.

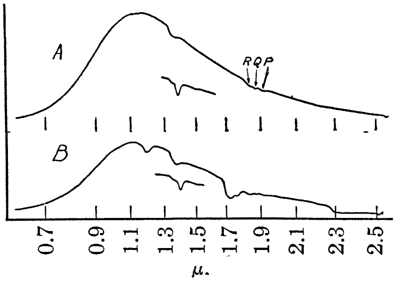


Fig. 13.—A, Intensity distribution; B, pentane.

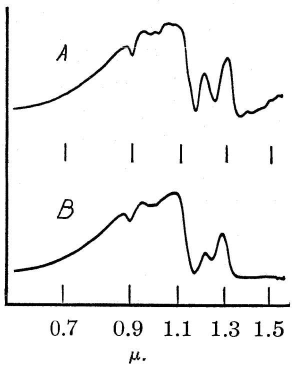


Fig. 14.—A, Acetaldehyde; B, propionaldehyde.

Several investigations made in the region beyond 2.5 μ include molecules

---

[2] Smith and Boord, This Journal, 48, 1512 (1926).

containing the carbonyl group. The extensive study made by Coblentz[3] includes several of these molecules. His records show in each case a strong band near 5.8 μ which he apparently refrains from definitely associating with the $=C=O$ pair because the paraffin hydrocarbons also show a weaker band at this position.

Marsh[4] pointed out that in an investigation made by Spence[5] upon a number of alkaloids the presence or absence of a strong 5.8 μ band marks a distinguishing feature between those molecules containing the carbonyl group and those which do not contain it.

Henri[6] concluded from his study of several aldehydes, ketones and acids that three bands at 8.2–8.5, 5.7–5.85 and 4.9 μ are produced by the $=C=O$ pair.

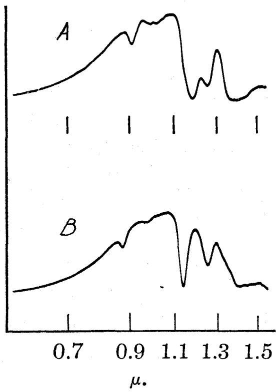


Fig. 15.—A, Butyraldehyde; B, benzaldehyde.

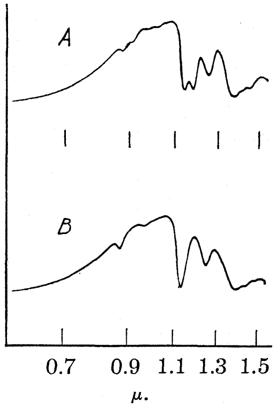


Fig. 16.—A, p-Tolualdehyde: B, cinnamaldehyde.

Bonino's[7] investigation of four homologous ketones was limited to the C–H band at 3.4 μ.

From the results of a study of twenty-five aldehydes and ketones Lecomte[8] concluded that a band occurring between 5.90 and 6.03 μ characterizes the $=C=O$ group, while a weaker one at 2.90–3.05 μ is its first overtone. (Lecomte's values are obviously consistently too high, as is evidenced by a comparison of the values in this and others of his papers with numerous determinations by various investigators.)

In his visible Tesla emission spectra of some aldehydes and ketones, Marsh[9]

[3] Coblentz, *Carnegie Inst.* Pub., No. 35 (1905).

[4] Marsh, *Phil. Mag.*, 49, 1206 (1925).

[5] Spence, *Astrophys.* **J.**, **39**, 243 (1914).

[6] Henri "Études de Photochimie," Gauthier-Villars, Paris, 1919.

[7] Bonino, *Gazz. chim. ital.*, 55, 335 (1925).

[8] Lecomte, *Compt. rend.*, 180, 1481 (1925).

[9] Marsh, *Phil. Mag.*, 49, 971 (1925).

found certain "blue bands" which showed a constant frequency separation of 172 mm.^{-1}. This frequency he associated with a molecular vibration which also gives rise under the proper conditions to the 5.8 μ infra-red absorption bands of these substances.

A conclusion by Bell[10] derived from his examination of the infra-red absorption of several tropine alkaloids is of interest. He is unwilling to conclude that the 5.8 μ band which he observed in those compounds containing the =C=O groups is a unique characteristic of this group inasmuch as the simple chain hydrocarbons also show absorption in the same region. Bell[11] still retains this attitude in his recent interpretation of the appearance of a strong 5.75 μ band in his spectra of seven organic carbonates.

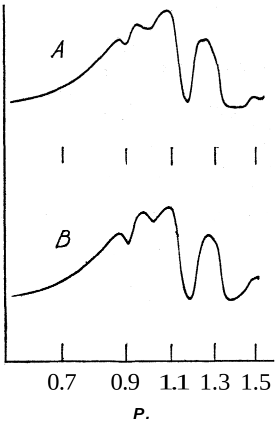


Fig. 17.—A, Acetone; B, methyl-n-propyl ketone.

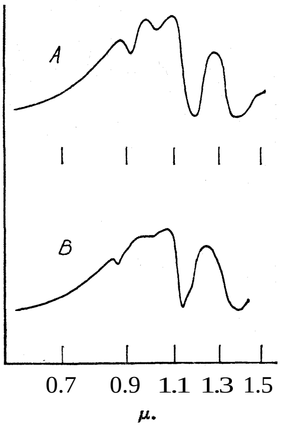


Fig. 18.—A, Methyl-n-amyl ketone; B, Acetophenone.

Bennett and Daniels[12] have recorded the absorption of acetic acid, mono-, di- and trichloro-acetic acids, methyl acetate and acetic anhydride in the regions 2–6 μ and 7–8 μ. They observed a strong band at 5.9 μ for acetic acid which progressively shifts to 5.75 μ upon successive substitutions of chlorine atoms. Their conclusion that this absorption maximum arises from the hydroxyl pair of the carboxyl group is not supported by the appearance of equally intense bands at 5.8 μ and 5.6 μ in their spectra of methyl acetate and acetic anhydride, respectively. It seems more probable that the bands in all six substances arise from the =C=O pair.

On the assumption that the 5.8 μ absorption maximum which is commonly observed is a fundamental band originating in a change of vibration

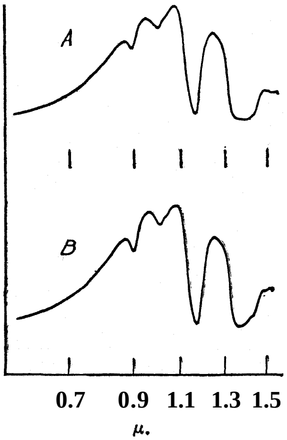
---

[10] Bell, *J. Pharm. Exptl. Therap.*, **29**, 533 (1926).

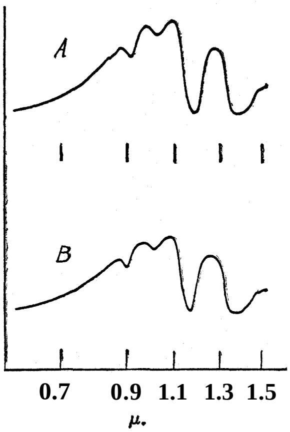
[11] Bell, THIS JOURNAL, 50, 2940 (1928).

[12] Bennett and Daniels, *ibid.*, **49**, 50 (1927).

of the $=C=O$ atoms and that the 2.9 μ band found by Lecomte is its first overtone, it might be reasonably anticipated that higher overtones could be found below 2.5 μ provided cells of sufficient thickness were used. Now in the records of the absorption by the 1-mm. layers of the compounds containing the carbonyl group, Figs. 1–13, eighteen out of twenty of these substances show definite absorption at 1.9–2.0 μ, which is not characteristic of ordinary hydrocarbons. The other two examples, *p*-tolualdehyde and benzophenone, are doubtful. If the bands do occur in their records they are weak. The uncertainty in these two instances is increased by the fact that the band in question falls upon the P branch of the 1.87 μ water-vapor band. The weakness of the band in benzophenone, assuming that it really is present, could possibly be explained by the fact that the molecular weight of this molecule is relatively high, thus reducing the number of $=C=O$ absorbing centers per cubic centimeter; and also perhaps by the fact that this substance was one of the two examined in carbon tetrachloride solution. Its weakness, or absence, in p-tolualdehyde is not so easy to understand.



Pig. 19.—A, Methyl acetate; B, ethyl acetate.



Pig. 20.—A, Butyl acetate; B, ethyl malonate.

The region 1.9–2.0 μ is the one in which a second overtone band of the 5.8 μ band would be sought. Because of the variation in the location of this longer wave length band as recorded by different observers, it is a little difficult to decide whether there is an exact integer relationship between it and the 1.9 μ band. A slight deviation from an exact one-to-three ratio between their frequencies would be anticipated as a result of numerous observations made upon infra-red absorption series. Thus the wave length of this possible harmonic band should be slightly greater than one-third of the wave length of the fundamental. A deviation comparable to the 1.5% variation from a 1:3 relationship found by Schaefer and Thomas[13] and calculated by Birge[14] between the fundamental carbon monoxide band at 4.67 μ and its second overtone at 1.57 μ mould be expected. The much larger variation, 4%, found by the writer[15] for infrared absorption bands produced by C–H anti N–H groups is doubtless due to the greater amplitudes of vibration resulting from the lightness of the hydrogen atom.

The inability to ascertain the exact nature of the overtone relationship existing between the 5.8 μ and the 1.9 μ bands is increased by the fact that the latter band appears double in a majority of the spectra. Whether this doubling has any bearing upon a similar phenomenon in many hydrocarbon bands[15] cannot be decided at this time.

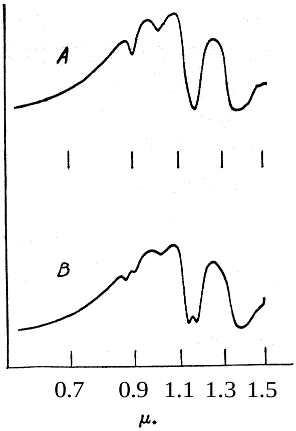


Fig. 21.—A, Ethyl propionate; B, ethyl benzoate.

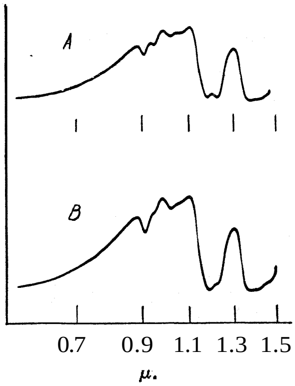


Fig. 22.—A, Ethyl ether; B, propyl ether.

As an example of the uncertainty which arises we may consider the spectrum of acetone, Fig. 4A. It shows prominent bands at 1.91 and 1.97 μ. Now the long wave length absorption maximum has been located by Coblentz[3] at 5.75 μ and by Henri[6] at 5.7 μ. Thus an exactly harmonic band would be expected between 1.90 and 1.92 μ. The question remains whether this overtone band is to be sought in the observed 1.91 μ or the 1.97 μ band or in their weighted mean. The writer inclines toward the latter point of view.

A third overtone of the 5.8 μ band would occur near 1.45 μ. The records of the 40-mm. cells, Figs. 14–23, show absorption at this point, indications of doubling appearing in several instances. Again, uncertainty

---

[13] Schaefer and Thomas, Z. *Physik*, 12,330 (1923).

[14] Birge, *Phys. Rev.*, 28, 1157 (1926).

[15] Ellis, *ibid.*, **33,** 27 (1929).

is introduced because of the proximity of the complicated 1.4 μ band characteristic of hydrocarbons.

A fourth overtone, if present, should occur near 1.16 μ. This again falls upon or near a C–H band. The asymmetry of the deep 1.14–1.20 μ absorption band in many instances indicates the possible presence of such an overtone.

A fifth overtone would be found near 0.97 μ. Such a band does appear in the records of the aldehydes. If it is present in many of the other curves it is either very weak or has shifted to merge with the 1.0 μ hydrocarbon band.

Absorption near 0.9, 1.0, 1.18, 1.4, 1.7 and 2.18 μ (benzene and phenyl radical), 2.3 μ (paraffins and alkyl radicals) is characteristic of hydrocarbons. In addition to these bands and those mentioned above as probably belonging to the carbonyl pair, there are other special features of these records which seem to be introduced by the presence of the carbonyl pair. Thus in the six aldehyde curves, Figs. 14–16, there appears a strong band at 1.25 μ. Again, in the records of most of the substances, excluding the three ethers, there is absorption near 2.15 p, in many instances the band being noticeably double. If there are other fundamental absorption bands assignable to the $=C=O$ group, as claimed by Henri, then combination bands obtained from these and the 5.8 μ band and its overtones might be expected in this shorter wave length region. Thus if we add the frequency of Henri's 8.3 μ band to the frequency of the 2.9 μ overtone of Lecomte we obtain a frequency of a band at 2.15 μ. Again, a combination of the 8.3 μ and our 1.45 μ band yields a value of 1.23 μ. These values are in good agreement with those mentioned above.

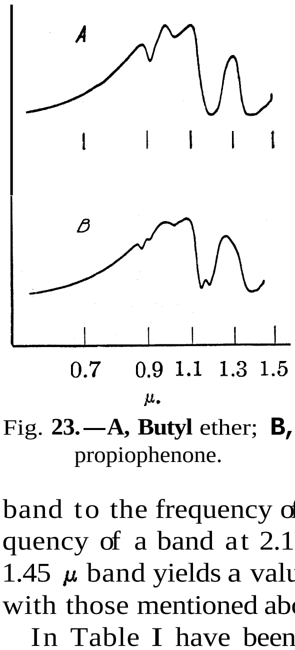


Fig. **23.—A, Butyl** ether; **B,** propiophenone.

In Table I have been assembled the values for the absorption bands which are here assumed to arise from the carbonyl group. Determinations by other investigators have been included also.

There are features of these spectra other than those apparently originating in the $=C=O$ pair which are of interest. Most of the remaining prominent absorption maxima are characteristic of hydrocarbons. The bands near 1.7, 1.2 and 0.9 μ can now fairly certainly be identified[15] as the first, second and third overtones, respectively, of a 3.3–3.4 μ band, all of which arise from oscillations of the carbon–hydrogen atom pair. They may be referred to as C–H bands. Bands near 1.0, 1.4 and 2.3 μ (or 2.18 μ) also always appear in the spectra of hydrocarbons and may be

TABLE I

ABSORPTION BANDS ASSIGNED TO THE $=C=O$ PAIR

Wave lengths in μ

Acetaldehyde	....	....	....	....	1 9 1 ...	1461.41	096	..	.. 1 2 4
Propionaldehyde	....	.	5 90L	2 93L	1 91 1 96	1 46 ..	.96	. . .	1 24
Butyraldehyde	....	....	5 90L	....	1.91?1.96	1 44 1.40	.98	.. ..	1.25
Benzaldehyde	....	5 97L	5 8H	. . .	1.92 1.99	1 45 1.42 1 41	.97	.. ..	1.25
p-Tolualdehyde	....	....	....	....	1 91?1 99 2 04?	1 46 1.42	.97	.. ..	1.25
Cinnamaldehyde	....	....	....	....	1 92 2.02	1.49 1 42	.97	.. ..	1 25
Acetone	5.75C,	5 7R	5 90L	2.90L	1 91 1.97	1.44	.96	2.15 2 18	..
Methylpropyl ketone	....	....	5 92L	2 90L	1 91 1.97	..	..	2.15218	..
Methyl-n-amyl ketone	....	.	....	....	1 91 1 97	..	..	2.152 18	..
Acetophenone	. . .	6 03L	5 8H	2 97L	1.91 2 01	..	..	.. ..	..
Propiophenone		....	6 03L	2 97L	1.91 2 01	..	..	.. ..	..
Benzophenone	. .	.	....	....	?	..	..	.. ..	..
Methyl acetate	. .	5 8C	5 8BD	....	1 91 1 93SB	1.42	..	2.12 2.16	..
Ethyl acetate	....	....	....	....	1 91 1 94	1.42	..	2 12 2.16	..
n-Butyl acetate	....	....	....	....	1 91 1.94	..	..	2.12 2 16	..
Ethyl malonate	....	....	....	....	1 91 1 94	..	..	2.14	..
Ethyl propionate	....	....	....	....	1 91 1 94 1 91SB	..	..	2.16	..
Ethyl benzoate	....	....	....	....	1.91 1.95	..	..	..	..
Acetylacetone	....	....	....	....	1.91	..	..	..	..
Quinone	....	....	....	....	1 90'	..	..	2.14	..

L = Lecomte, ref. 8; H = Henri, ref. 6; C = Coblentz, ref. **3;** SB = Smith and Boord, ref. *2;* BD = Bennett and Daniels, ref. 12.

referred to as hydrocarbon bands. Their origins are probably more complicated than those giving rise to the 3.4 μ fundamental and its harmonics. A possible interpretation of their origins, which further study may show to be only partially correct, has already been suggested by the writer.[1b]

The author[15] has already commented upon the doubleness of the C–H bands of certain compounds, suggesting that this doubleness may arise from two types of C–H linkages. Such an hypothesis is supported by the conclusions of Mrs. Lonsdale[16] in her critical study of the physical evidences pointing toward an anisotropy of the carbon atom. She has concluded that carbon will in general exhibit two each of two types of valency. This doubleness is evident in the 1.75 μ band of many of the alkyl compounds. It always appears when a methyl or ethyl group is present and sometimes when a propyl radical occurs. The breadth of the band when higher radicals are used, for example butyl, suggests that the doubleness is still there but that it is partially obscured. The 1.68 μ band, which appears clearly separated from the 1.75 μ doublet in the spectra of alkyl derivatives in which the radical is relatively light, but which merges into this latter band when the alkyl radical is heavy, seems to be a characteristic feature of paraffins and alkyl radicals. Its exact nature is not understood.

[16] Lonsdale, *Phil.* Mag., **6,433** (1928).

The two molecules benzophenone and quinone, containing aryl groups without alkyl groups, show a single band at 1.68 μ corresponding to the alkyl doublet at 1.75 μ. Those compounds containing both types of radical show the alkyl doublet and single aryl band clearly separated.

The resolving power of the instrument is probably insufficient to reveal a doubling of the 1.2 μ and the 0.9 μ alkyl C–H bands if it exists. A distinct separation in these bands, however, is found between the alkyl and aryl components.

An unexpected and widely separated doubling of the 1.2 μ and the 0.9 μ bands occurs in the spectra of the three ethers. Since the changes in the intensity ratio of the two components are similar as one goes from ethyl ether to n-butyl ether, it seems that both members are C–H bands. The only explanation which the author can offer for this doubling is a possible weakening of the C–H bonds in the cases of carbon atoms adjoining the oxygen atom.

The increased resolving power obtained in these records has revealed the fact that the 2.18 μ hydrocarbon band of the phenyl radical is double. A new record taken of benzene, not reproduced in this paper, shows a corresponding doubling.

The writer wishes to acknowledge the assistance of Mr. Charles Shaw in a portion of this investigation.

Summary

1. The infra-red absorption spectra below 2.5 μ have been recorded for a group of aldehydes, ketones, esters and ethers.

2. An absorption band, often double, between 1.9 and 2 μ is interpreted as a second overtone of a prominent 5.8 μ band previously recorded by many observers. Both are assigned to the carbonyl group.

3. Evidence pointing toward the existence of third, fourth and fifth overtones of the 5.8 μ band is found near 1.45, 1.16 and 0.97 μ in the spectra of some of the compounds.

4. Features characterizing hydrocarbons and their derivatives are found in these spectra at positions where they were anticipated.

LOS ANGELES, CALIRORNIA

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, PRINCETON UNIVERSITY]

BUDDE EFFECT IN BROMINE AND CHLORINE

BY GEORGE B. KISTIAKOWSKY

RECEIVED JANUARY 2, 1929 PUBLISHED MAY 6, 1929

Some time ago[1] the writer described experiments intended to show that extensive drying produces neither appreciable fluorescence in chlorine on illumination, nor a change in its absorption spectrum. That the absorption spectrum remains unchanged on drying was found, independently and simultaneously, by Miss Kornfeld and Steiner.[2] The existing literature,' on the other hand, seemed to indicate that the Budde effect, or the heat expansion of halogens on illumination, decreases when the halogens are subjected to a more or less thorough drying. These divergent observations are difficult to reconcile and it was tentatively suggested that, while the primary photochemical process in halogens is a dissociation into atoms in the way suggested by Franck, the secondary process, a homogeneous recombination of atoms, which contributes mainly to the heating of the gas, requires the presence of water vapor, being otherwise slow. In this case the halogen atoms in highly dried gases will have time to diffuse to the walls before recombining; they will be cleaned up there and will recombine in a wall reaction, the heat liberated being conducted away by glass and little heating of the gas being produced. The present experiments were intended to test this suggestion but, first of all, to investigate generally the observations obtained elsewhere on the influence of water vapor on Budde effect. While these experiments were being conducted, Brown and Chapman[3] published their observations showing that in a mixture of bromine vapor and air very extensive drying by phosphorus pentoxide lasting over a period of several months does not produce any change in the magnitude of the Budde effect. These experiments are quite conclusive by themselves, but they do not touch on the problem of whether the Budde effect in bromine from which all impurities, particularly such as oxygen, have been removed, might not still show a dependence on the presence of water vapor. To settle this last problem, for chlorine as well as for bromine, is the object of the investigations reported here.

Experimental Details

To study the Budde effect, a cylindrical Pyrex tube 23 × 3.5 cm. with polished sealed-on end-plates was used. It was connected to an all-glass manometer, a thin caved-in glass bulb with a long pointer being used. The movements of the pointer were observed in a microscope, the sensitivity of the system being *ca.* 10 divisions on the ocular scale per 1 mm. of mercury. Since such devices usually do not withstand large pressure differences, the whole manometer was sealed in a glass enclosure, which com-

---

[1] Kistiakowsky, THIS JOURNAL, 49, 2194 (1927).

[2] Kornfeld and Steiner, Z. *Physik,* 45, 385 (1927).

[3] Brown and Chapman, J. *Chem. Soc.*, 133, 560 (1928).

municated, through a by-pass, with the illumination vessel. The whole was evacuated, baked out and filled with the halogen vapor. The outside of the manometer, however, could be disconnected, before the illumination experiments, by heating and collapsing a constriction in the by-pass. Inside the illumination vessel along its axis and at a distance of a few mm. from the side wall was suspended a loop of an almost hair-fine glass capillary through which a platinum wire was drawn. The wire acted as a resistance thermometer, its leads being carried to the outside of the vessel. The construction was such that the halogen vapors came in contact with glass only, no metal parts being exposed. **A** short tubing connected with the illumination vessel an inner, magnetically operated, seal which opened to a space of about 1-cc. volume filled with water vapor of atmospheric pressure.

The drying of bromine was carried out with the aid of phosphorus pentoxide. This latter was purified by a double distillation in a stream of pure oxygen and afterward by a double distillation in high vacuum. It was then distributed, by a careful sublimation in vacuum, over the walls of two wide U-tubes and their connecting tube. Bromine of C. P. grade was further purified and moderately dried by the standard chemical methods. It was then distilled twice in vacuum, the middle sections only being retained and finally was admitted to the phosphorus pentoxide tubes by breaking an inner seal. The quantity of bromine thus introduced was relatively small and it wetted only a fraction of the P_2O_5-covered surface. By cooling different parts of this surface bromine was distilled back and forth, this operation being continued for forty-eight hours. Later, an inner seal separating the illumination vessel and manometer system from the phosphorus pentoxide tubes was broken and bromine vapor admitted into the former. This inner seal was on the opposite end of the P_2O_5-tubes from that at which the undried bromine originally entered. The illumination vessel and manometer system, as well as the P_2O_5-tubes, prior to filling were baked out in vacuum for about twenty hours. The temperature was raised first to 500° for two hours and maintained at 350" the rest of the time.

Chlorine taken from a half empty tank was dried by repeaied distillation in vacuum from a bath of melting ethyl bromide (—119"). In the first of the series of three experiments an attempt was made to remove traces of oxygen present by an initial prolonged bubbling of pure hydrogen through liquid chlorine at —80°. In the other two experiments a larger quantity of chlorine was condensed from the tank, about four-fifths of it was boiled away under reduced pressure and only the first half of the remaining fraction was used for the succeeding vacuum distillations. The distilling train, allowing four distillations, was divided by an inner seal into two sections with separate pumping aggregates. Inner seals separated the train from the vessel into which chlorine was originally condensed and from the illumination vessel aggregate.

It was intended to test the dryness of chlorine by the sensitivity of the hydrogen–chlorine mixture to light and the apparatus contained, therefore, besides the parts described, four small cylindrical tubes sealed in parallel which also could be filled with dry chlorine. These tubes were separated by an inner seal from the hydrogen-drying section of the apparatus. The drying of purified hydrogen was carried out by allowing it to pass through a long spiral (4-mm. tubing, 50 cm. long) immersed in liquid air. The rate of flowof hydrogen through the spiral was adjusted by a capillary and amounted to **250** cc. in twenty hours. Dried hydrogen entered in the first experiment a half-liter flask which was evacuated together with the rest of the apparatus. In the second experiment the flask was replaced by a wide glass tubing forming a closed circle. The lower part of it was immersed in liquid air and one side was gently heated (to *ca.* 100°) so that hydrogen entering from the spiral was circulated continuously over liquid air. In the third experiment the flask was replaced by a vessel of a cylindrical shape which **was** completely immersed in liquid air for forty-eight hours.

On filling the four reaction tubes with chlorine at *ca.* **0.3** atmosphere pressure, they were sealed off from the chlorine side of the apparatus and were connected, by breaking an inner seal, to the hydrogen section which contained gas at about **0.5** atm. pressure. Chlorine was then frozen out by liquid air in each of the vessels and they were finally completely sealed from the apparatus.

The baking out of the whole apparatus was done in an electric furnace, the temperature, as in the case of bromine, being raised first to 500° and maintained later at **350".** The baking was continued for twenty-four hours in the first experiment and was extended to ten days in the last one. Here the heating was interrupted on the fifth day and all constrictions, to be sealed off afterward, were heated to the softening point and allowed to collapse almost completely; the baking was then resumed. The degassing was rather thorough in this experiment, as is shown by the fact that on the tenth day the McLeod gage, sensitive to less than 10^{-5} mm. of mercury, showed no measurable pressure after the apparatus was shut off from the pump overnight, while being heated to **350°.**

For the study of the Budde effect a carbon arc burning on **20** amp. and a system of lenses and diaphragms was used by means of which a parallel beam of light of about **2** cm. diameter was separated. In front of the illumination vessel, which was rigidly fastened to the optical bench supporting the arc and the lenses, was arranged a shutter to make possible a rapid succession of illumination and darkening of the vessel.

Experimental Results

With the apparatus described three samples of bromine and three of chlorine were prepared and tested. The general procedure was to take a simultaneous series of the glass manometer and of the platinum resistance readings with the shutter alternately closed and opened, then to break the inner seal separating the water vapor compartment and take a new series of readings. Under no circumstances could even the slightest difference exceeding the experimental error be observed between the two series of readings. In the third experiment on bromine a second inner seal was attached to the illumination vessel. It separated a small evacuated volume filled with phosphorus pentoxide prepared in the same manner as the materials used in the initial drying of bromine. After the first series of readings with this bromine, the seal separating the phosphorus pentoxide was broken and the latter transferred, by shaking, into the illumination vessel. It was left there for ten days, occasional readings being taken. Then the seal separating the water vapor was broken and readings were taken immediately after and on the next day. As an example of the nature of readings bbtained these series with bromine No. **3** are reproduced in Table I.

Under "glass-manometer" are given the deflections of the pointer in scale divisions of the microscope scale as caused by sudden changes from dark to light and back; under "Pt-resistance thermometer" the deflections in scale divisions of the galvanometer, which, together with a Mueller type bridge, was used to measure the resistance of the platinum wire. The temperature change and the expansion of the gas on illumination, as measured here by the two devices, agree fairly well. Ten divisions on

TABLE I

BUDDE EFFECT IN BROMINE

	Dry bromine	P_2O_5 admitted	10 days later	H_2O admitted	1 day later
Glass-manometer	+11, −10; +10, −10; $11, − 9; $10, − 9; +10, − 9; + 9, − 9; $11, − 9; +10, − 9; av. 9.7	av. 9.3	av. 10.1	av. 9.9	av. 9.3
Pt-resistance thermometer	+24, −22; +21, −20; +21, −20; +22, −20; +20, −20; +19, −20; +23, −20; +20, −21; av. 20.8	av. 21.1	av. 21.7	av. 22.0	av. 20.6

the microscope scale corresponded very nearly to 1 mm. of mercury or to approximately one degree temperature change of bromine vapor which was used at 300 mm. pressure. The thermometer had a resistance of 5.9 ohms and the galvanometer sensitivity was 18 scale divisions for 0.01 ohm. The deflection of 21 scale divisions thus corresponds roughly to 0.7° temperature change. The difference is well accounted for by the facts that only about nine-tenths of the total length of the wire in the thin capillary could be rapidly heated by the gas and that the whole wire, being outside of the actual path of the light beam, was in a somewhat cooler part of the gas.

Table I, which is quite typical of the results obtained, shows quite definitely that the Budde effect in bromine is left entirely unchanged by drying or moistening of the halogen. Thus, the experiments of Lewis and Rideal,[1] who claimed that a proportionality exists between the concentration of the water vapor and the magnitude of the Budde effect, must be incorrect. It might be suggested, of course, that a "more thorough" drying would reveal an influence of water vapor. However, the experiments of Brown and Chapman[s] are against such suggestion. Moreover, it should be pointed out here that the drying now employed must have been quite efficient. With a magnifying glass, one could see a slight trace of moisture on the first grains of the drying agent where bromine first entered the phosphorus pentoxide tubes. The moisture, which could be noticed only in this location, indicates that the phosphorus pentoxide employed was active and had extracted the main fraction of the water vapor present already within the short time of contact with bromine vapor when this was being distilled under low pressure into the phosphorus pentoxide tubes.

The experiments with chlorine yielded the same result as those with bromine: no change in Budde effect could be observed on drying. Comparing the relative care taken in drying and purifying chlorine by Coehn and Jung[1] and in the present experiments, one might conclude that the halogen was in about the same state of dryness in both sets of experiments.

However, the first of the experiments described here yielded chlorine–hydrogen mixtures which all reacted very rapidly in visible light. The experiment, therefore, was repeated twice more, each time new precautions being taken, of which a part have been mentioned before. Still, the result was the same; the photochemical reactivity of the gases was not diminished by drying. On the other hand, a critical analysis of the drying method employed fails to indicate any systematic sources of moisture in chlorine. Another explanation of the failure to prepare dry chlorine–hydrogen mixtures seems to be very likely therefore. As has been pointed out to the writer by Dr. R. N. Pease of this Laboratory, according to his experience, hydrogen reduces Pyrex glass quite readily at the temperature of its softening point. Since the last sealing of the reaction tubes in our experiments has to be undertaken with an atmosphere of hydrogen inside, it is more than likely that a sufficient quantity of water vapor is produced to cause photochemical reactivity of the gases. The quantity of water vapor required for this can be estimated, on the basis of experiments of Coehn and Jung,[1] to be of the order of 10^{-10} g. for the 10-cc. tubes employed. An action of chlorine on Pyrex glass, also followed by evolution of water, is very unlikely and it can be claimed, therefore, that the chlorine here prepared—so long as it was not mixed with hydrogen—was of the same degree of dryness as that prepared by Coehn and Jung. The latter evidently avoided our difficulties with hydrogen–chlorine mixtures by the use of soft glass.

Summary

1. No change in Budde effect could be observed on purifying and carefully drying bromine and chlorine.
2. It is pointed out that dry mixtures of hydrogen and chlorine cannot be prepared in Pyrex glass, since the latter is reduced at its softening point by hydrogen with formation of water.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND OF STANFORD UNIVERSITY]

CYCLOHEXANOL AND THE THIRD LAW OF THERMODYNAMICS[1]

BY KENNETH K. KELLEY[2]

RECEIVED JANUARY 2, 1929 PUBLISHED MAY 6, 1929

All statements of the third law of thermodynamics with the exception of that of Eastman[3] agree that the entropies of two crystalline forms of the same substance may both be taken as zero at the absolute zero of temperature. The only test of this statement which has been made with sufficient accuracy to warrant consideration is for the two crystalline modifications of tin. Lange[4] has measured the specific heat of white tin down to 9.6°K. and of gray tin to 15.5°K. and Bronsted[5] has calorimetrically determined the heat of transition. The entropy of transition at 292°K. from Lange's data and the third law is 1.77 E. U. while Bronsted's measurement gives 1.83 E. U., a very good agreement. However, the gray tin which is transformed into the white on cooling goes back to the gray modification, thus making it necessary to use a sample of white tin in the specific heat measurements in a different physical state from that obtained by carrying the gray tin through the transition point. This probably causes only a very slight error. For a more complete discussion of the tin transition the reader is referred to that of Simon.[6]

The present paper presents data on two crystalline forms of cyclohexanol. The heat capacity curves for both forms were obtained down to about 13.5°K. and the heat of transition calorimetrically determined using the same sample of material and the same apparatus throughout. The apparatus and methods used have been described previously.[7]

Purification of Material.—The cyclohexanol was an Eastman Kodak Company product. It was dried with anhydrous sodium carbonate, decanted off and fractionally distilled twice. Further purification was obtained by fractional crystallization. The portion used for the measurements (about 50 cc. in volume) had a boiling range of 160.9–161.0° (760 mm.) and density $d_4^{22.2} = 0.9459$. It was kept in a sealed bottle until placed in the calorimeter.

The Measurements.—The specific heats in 15" calories per mole are given in Table I and shown graphically in Fig. 1.

When cyclohexanol is cooled slowly it undergoes a transformation at

---

[1] The experimental work of this paper was done at the University of California.

[2] National Research Fellow in Chemistry.

[3] Eastman, THIS JOURNAL, 46, 43 (1924).

[4] Lange, *Z. physik. Chem.*, 110 (Nernstband), 343 (1924).

[5] Bronsted, *ibid.*, 88, 479 (1914).

[6] Simon, "Handbuch der Physik," Julius Springer, Berlin, 1926, Vol. X, p. 372.

[7] Kelley, THIS JOURNAL, 51, 180 (1929).

TABLE I
SPECIFIC HEATS OF CYCLOHEXANOL
1 mole = 100.1 g.

T, °K.	C_p, cal./mole
Low Temperature Form	
16.09	1.381
19.92	2.294
23.38	3.097
27.28	3.994
30.91	4.797
35.00	5.676
39.30	6.559
43.45	7.270
47.83	7.979
52.35	8.631
57.60	9.440
63.07	10.16
68.15	10.52
77.06	11.49
85.11	12.26
93.38	13.16
101.84	13.98
111.43	15.06
120.19	16.18
122.14	16.55
128.49	16.95
136.76	17.56
145.11	18.46
153.23	19.23
161.03	19.87
168.86	21.01
181.33	22.60
189.08	23.62
197.30	25.02
206.21	26.13
215.81	27.25
225.02	29.04
234.35	29.85
241.38	32.05
245.11	32.85
248.57	35.03
248.69	35.12
251.80	38.76
252.98	38.03
254.74	45.07
257.28	60.93
258.95	99.3
260.19	157
260.25	154
261.32	198
261.98	315
263.19	342
263.71	439
264.16	350
265.30	79.3
High Temperature Form	
15.25	1.919
18.75	2.838
22.11	3.701
25.69	4.503
29.07	5.281
33.00	6.066
37.32	6.946
41.45	7.589
45.70	8.258
50.09	8.887
59.70	10.25
69.91	11.46
75.40	12.17
85.20	13.28
93.42	14.25
101.31	15.12
108.64	16.11
109.63	16.21
118.03	17.42
119.15	17.50
126.81	18.55
135.07	19.92
142.68	22.21
145.56	23.70
148.21	27.73
149.22	27.94
150.45	28.39
153.02	28.66
155.56	28.78
158.99	28.76
212.80	32.98
217.31	33.28
231.02	34.50
235.50	35.26
244.13	36.34
252.03	37.31
260.41	38.55
264.84	39.39
267.95	39.98
271.96	40.70
280.01	41.90
Liquid	
298.15	49.96
298.68	49.90

about 263.5°K. If cooled with sufficient rapidity the high temperature form is supercooled and may be taken down to the temperature of liquid hydrogen with no difficulty. The nature of the specific heat curves in the transition region may be seen better in Fig. 2.

On warming, the supercooled high temperature form exhibits regular specific heats up to about 135°K. Here there is a very sharp rise similar to that encountered for glasses which are also supercooled forms of matter. This rise is over at 150°K. At about 160°K. the supercooled form on warming changes spontaneously into the low temperature form, This change always occurs at very nearly the same temperature, which is again similar to the behavior of glasses. Between 160 and 210°K. no measurements could be made on the high temperature form for this reason.

The two measurements between 210 and 220°K. were made with the substance very slowly changing over into the low temperature form and for this reason these two results may be somewhat low. Above 230°K. the high temperature form had considerable apparent stability and no difficulty was found in making measurements from here up to the melting point. This was fortunate because it meant that results on this form could be obtained throughout the region in which the low temperature form was undergoing the transition to the high. It is interesting to note that in the case of white tin Lange found no such sharp rise as that occurring around 140° in the present work. However, he omitted two large temperature intervals, from 57 to 92°K. and from 101 to 286°K. It is in the latter interval that such a phenomenon might be expected.

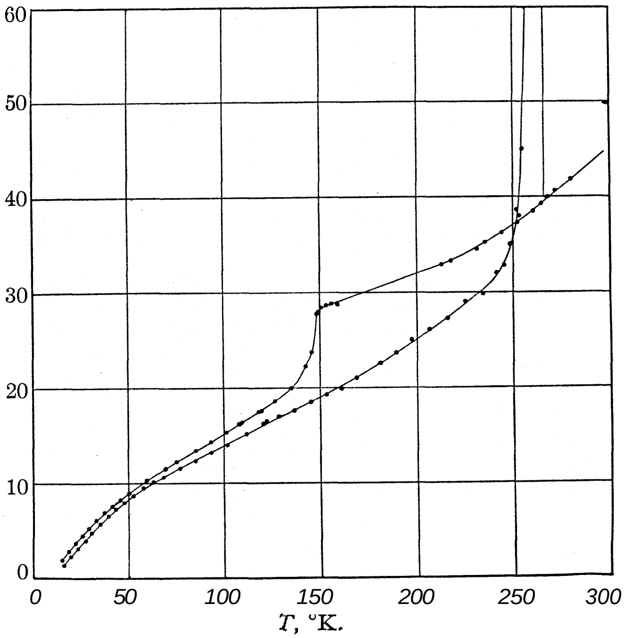


Fig. 1.—The specific heat of cyclohexanol in cal. per mole.

The low temperature form up to the transition region gave normal specific heats. The transition is apparently of the ammonium chloride type as is also the methyl alcohol transition." It is not possible to say just how great an effect the small amounts of impurities present have on the nature of the specific heat curve in this region.

The Temperature and Heat of Transition.—The mean temperature of the transition was found to be 263.5°K. and the heat of transition was also measured, the results obtained being given in Table II. By heat of transition here is meant the heat absorbed per mole in passing through the transition region in excess of the energy $\int_{T_1}^{T_2} C_p\mathrm{d}T$, under the "normal" heat-capacity curves extrapolated to 263.5°K. This is admittedly somewhat arbitrary but can cause no appreciable error in the entropy calculations to follow.

Table II

Heat of Transition in Cal. per Mole

T, °K. (average)	1st result	2nd result	Mean
263.5	1963	1957	1960

The Temperature and Heat of Fusion.—Richards and Shipley[8] have measured the temperature of fusion of a very pure sample of cyclohexanol as 297.0°K. Considerable difficulty was found in obtaining the temperature of fusion of this substance in the calorimeter because of its very low heat of fusion. The best value obtained was 0.2 or 0.3 of one degree lower than that obtained by Richards and Shipley. However, their value is undoubtedly the better since the substance absorbs water very readily and consequently in filling the calorimeter a slight amount of moisture may have been introduced. Therefore the heats of fusion given in Table III have been corrected to 297.0°K.

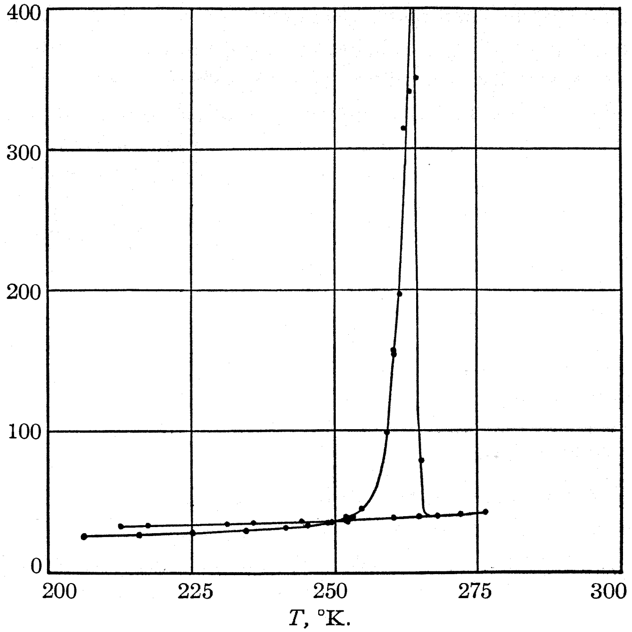


Fig. 2.—The specific heat of cyclohexanol in cal. per mole in the transition region.

---

[8] Richards and Shipley, This journal, 41, 2002 (1919).

TABLE III

HEAT OF FUSION IN CAL. PER MOLE

T, °K.	1st result	2nd result	Mean
297.0	408	404	406

The heat of fusion was recently obtained by Cauquil[9] by dissolving the crystalline and liquid forms at the same temperature. The value so obtained is 427 cal. per mole which, considering the method used, agrees as well as could be expected with the present value.

Accuracy of Measurement.—The specific heat measurements, except for those in the transition region between the low and high temperature forms which are not used in the entropy calculations, are considered to be in error on the average by not more than 0.5%. A more detailed discussion of the accuracy of measurement given before[7] will also apply here. The heat of transition also is not considered to be in error by more than 0.5%. The heat of fusion may easily be in error by 1%.

Entropy Calculations.—The entropy changes were calculated in the usual manner. Extrapolation below 13.5°K. was made by means of Debye functions with $\Theta = 112$ for the low temperature form and $\Theta = 84$ for the high. The extrapolated values, 0.27 and 0.58 E. U., respectively, are small and cannot be greatly in error. This may be readily seen from a comparison of these results with limiting values obtained by other means and given in Table IV.

TABLE IV

VALUES OF $S_{13.5}$ (EXTRAPOLATED)

Low temperature form	0.25	0.27	0.38
Method	aT^3	Debye	aT^b
High temperature form	0.49	0.58	0.80

The T^3 law applied below 13.5°K. must certainly give results which are too low since neither form has a low enough specific heat at 13.5°K. for this law to apply. The T^3 law, however, should apply at lower temperatures theoretically and has been found to do so experimentally for one organic substance, glycerin.[10] Fitting the lower end of each curve by an equation, $C_p = aT^b$, and using this as a basis of extrapolation should give too high results since $b = 2.38$ for the low temperature form and 1.89 for the high in the neighborhood of 13.5°K.

In Table V are given the results of the entropy calculations. Under I are given the entropy changes in passing from 0°K. to 298.1°K. starting with the low temperature form, transforming to the high temperature form at 263.5°K. and to the liquid at 297.0°K. Under II are given the corresponding values starting at 0°K. with the high temperature form which is carried up to the melting point and changed to liquid.

---

[9] Cauquil, *Compt. rend.*, 180, 1207 (1925).

[10] Simon and Lange, *Z. Physik*, 38, 227 (1926).

TABLE V

RESULTS OF ENTROPY CALCULATIONS

I			II		
(0–13.5) extrap. ($\Theta = 112$)	0.27		Extrap. ($\theta = 84$)	0.58	
(13.5–263.5) crystals	33.55		Crystals	40.32	
(1960/263.5) transition	7.44		.....	...	
$S_{263.5}$	41.26	± 0.25		40.90	± 0.25
(263.5–297.0) crystals	5.02		Crystals	5.02	
(406/297.0) fusion	1.37		Fusion	1.37	
(297.0–298.1) liquid	0.17		Liquid	0.17	
$S_{298.1}$	47.8	± 0.3 E. U.		47.5	± 0.3 E. U.

Discussion

If the entropies of the two crystalline forms at 0°K. are the same, then it follows that the entropy change corresponding to the warming of the substance from 0°K. to any temperature above the transition is the same for both possible paths. In making the calculations for Table V it was convenient to obtain the total heat of transition and assign it to a "mean" temperature for the purpose of calculating the entropy of transition. Since this has been done it is now convenient to compare the entropies at this point, 263.5°K., also. The values for the two paths are, respectively, 41.26 and 40.90 E. U., a difference of 0.36 E. U. Each of these values may be in error by ±0.25 E. U., so that this difference is within the upper limit of the experimental error and consequently in this case, as in the case of tin, the only conclusion which can be drawn is that both crystalline forms have the same entropy at 0°K. in agreement with the third law of thermodynamics.

The Free Energy.—The free energy of formation from the elements may be calculated by means of the equation $\Delta F = \Delta H - T\Delta S$.

The heat of combustion of solid cyclohexanol at 291°K. has been measured by Richards and Davis.[11] Their value when corrected to 15° calories gives 889,700 cal. per mole at constant pressure. From this value the heat of combustion of liquid cyclohexanol at 298.1°K. may be calculated by means of the specific heats of the substances involved and the heat of fusion of cyclohexanol. It so happens that the effect due to differences in the specific heats almost exactly counterbalances the heat of fusion and we have, therefore, 889,700 cal. per mole for the heat of combustion of liquid cyclohexanol at 298.1°K.

Making use of the values for the heats of combustion of graphitic carbon and of hydrogen previously adopted,[7] $\Delta H_{298.1}$ is found to be −85,840 cal. per mole.

Using 47.7 E. U. as $S_{298.1}$ for liquid cyclohexanol and the entropies of the elements,[7] $\Delta S_{298.1}$ is −162.2 E. U.

Therefore, $\Delta F_{298.1} = -37{,}500$ cal. per mole.

---

[11] Richards and Davis, THIS JOURNAL, 42, 1599 (1920).

Summary

1. The specific heats of two crystalline forms of cyclohexanol were measured down to about 13.5°K.
2. The "mean" temperature and heat of transition between the two crystalline modifications were obtained.
3. The heat of fusion of cyclohexanol was measured.
4. The entropy calculations show that both crystalline forms have the same entropy at 0°K. within the limits of experimental error.
5. The entropy and free energy of liquid cyclohexanol at 298.1°K. have been calculated.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEW HAMPSHIRE]

THE PREPARATION OF PHOSPHENYL CHLORIDE

BY J. A. C. BOWLES AND C. JAMES

RECEIVED JANUARY 4, 1929 PUBLISHED MAY 6, 1929

Since derivatives of phosphenyl chloride have been desired from time to time during rare metal research, it was decided to investigate certain methods involved in the preparation of this substance with the hope of finding some suitable and convenient procedure.

The cheapest method appeared to be that of passing vapors of benzene and phosphorus trichloride repeatedly through a red-hot tube. The equipment required was very similar to that employed in the earlier method for the preparation of diphenyl. After giving this method a thorough trial it was discarded owing to the fact that such a long time was required to produce a small quantity of the product. It appeared to the workers that without doubt a considerable amount of the phosphenyl chloride was decomposed owing to the long heating as it passed through a considerable length of the red-hot quartz tube. It therefore seemed desirable to use an apparatus similar to that described in the preparation of diphenyl,[1] in which a glowing ribbon of nichrome was suspended in an atmosphere of benzene vapors. In this case the difficulty was to find a suitable ribbon or filament which would withstand the action of the vapors. The only material which resisted attack and fusion was a large carbon filament which was very carefully removed from a large and antiquated electric light bulb. Unfortunately in this case the filament kept gradually increasing in diameter due to the deposition of carbon, thereby requiring a gradual increase in current throughout the run. It was noticed, however, that much better yields were obtained than by the previous method.

---

[1] Lowe and James, THIS JOURNAL, 45, 2666 (1923).

The writers found that equipment which was transparent and which allowed the product to be quickly removed from the hot surface gave the best yields since the process could be more easily controlled by observation. The next change made in the diphenyl equipment was the substitution of the ribbon by a heating unit which was unattacked by the vapors in the reaction chamber. The heater which was tried out consisted of a winding of nichrome protected by a quartz tube. This type of heating unit required a different kind of reaction chamber, of a form not unlike that of a common condenser jacket. A study of the accompanying figure will give a better idea of the apparatus. The mixture of benzene and phosphorus trichloride was placed in flask A which is connected to the reaction chamber B by means of a rubber stopper. The upper outlet of the reaction chamber was connected to a reflux condenser. This connection should either be sealed or else a ground joint, since rubber tubing must be changed after every run. The heating element is placed in the interior central portion of the quartz Tube CC which is made tight by alundum cement over a few turns of asbestos rope. Carbon dioxide was admitted to the reaction chamber through the small Tube D. The reaction chamber, dimensions 60 cm. X 15 cm., was made of Pyrex glass.

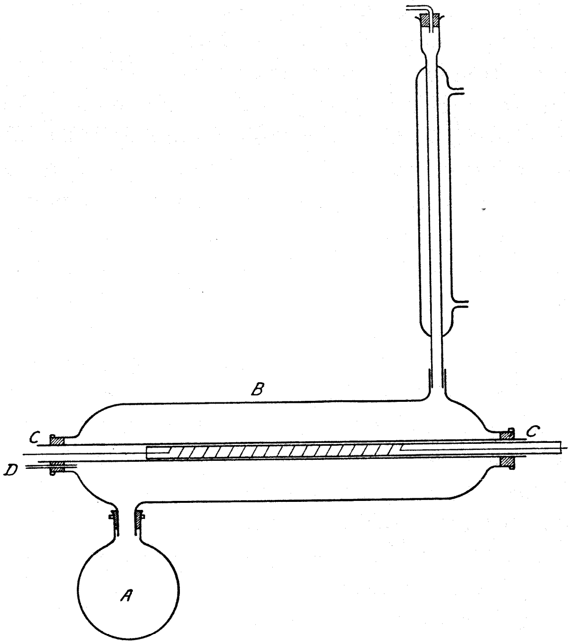


Fig. 1.

In commencing the operation, the liquid in A was heated until all the air in the reaction chamber had been displaced by vapor. At this point the heating current was turned on and the temperature of the quartz tube raised to a good red heat, care being taken to keep the temperature below carbonization. Under the right conditions the phosphenyl chloride could be observed flowing back to the flask along the bottom of the reaction chamber, the temperature of the latter being too high to allow much of the benzene and phosphorus trichloride vapors to condense. While no attempt was made to determine the maximum yield for an eight-hour run, it appeared that under the best conditions at least one kilo should be obtained *without any carbonization* with an equipment of this capacity.

This reaction chamber may be applied to other reactions where the vapor is heated to some definite temperature and where the reacting substances have similar boiling points. An interesting test was made in the case of the production of acetamide from acetic acid. The latter was just saturated with dry ammonia gas at the boiling point. This crude ammonium acetate was placed in the flask A and boiled while the temperature of the quartz tube was raised to 245° on the inside. As soon as the odor of acetic acid appeared at the top of the air condenser attached to the upper outlet of the reaction chamber, ammonia gas was slowly admitted through the small Tube D. When the speed of the ammonia gas was correctly adjusted practically nothing but steam was given off at the top of the condenser. The temperature of the escaping vapors was maintained at about 101°. At the end of a three hours' run it was found that the contents of the flask solidified to a mass of crystals on cooling. Fractional distillation showed that the product consisted almost entirely of acetamide. Under these conditions practically the theoretical amount of acetic acid was converted into acetamide.

In conclusion, it may be said that plans are being made to try out certain other reactions, involving this heating and cooling effect, and also the use of catalysts under such conditions.

DURHAM, NEW HAMPSHIRE

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 206]

THE POTENTIAL OF INERT ELECTRODES IN SOLUTIONS OF SULFUROUS ACID AND ITS BEHAVIOR AS AN OXIDIZING AND REDUCING AGENT

BY ARTHUR A. NOYES AND HAROLD H. STEINOUR

RECEIVED JANUARY 8, 1929 PUBLISHED MAY 6, 1929

I. Introduction

Certain reducing substances such as sulfurous acid, formic acid or oxalic acid show in their chemical behavior a much smaller reducing power than that calculated from the free-energy changes attending their conversion into their ordinary oxidation products (sulfuric acid or carbon dioxide and water). This is especially well known in the case of sulfurous acid, whose chemical reducing power is much less than corresponds to the potential (—0.14 volt) calculated for the conversion of SO_2(1 atm.) to SO_4^{--} (1 m.) in the presence of H^+ (1 m.).

The probable nature of the electrode process in a sulfite cell had been considered by Carter and James.[1] In view of the obvious discrepancy with the calculated sulfite–sulfate potential they attributed the observed potential to the tendency of the sulfur dioxide to be reduced rather than oxidized. The reduction product might be sulfur, but since their experiments showed that the addition of sulfur to the electrode vessel did not improve the constancy or reproducibility of the potential (which varied over 0.05 volt), they concluded that an intermediate reduction product of sulfurous acid was concerned. This product they considered to be probably dithionous acid,[2] $H_2S_2O_4$, since their experiments showed that this acid was produced by the cathodic reduction of sulfurous acid in acid solution.

---

[1] Carter and James, *J. Chem. Soc.*, 125, 2231–2240 (1924).

[2] This acid of formula $H_2S_2O_4$ is called by many authors hydrosulfurous acid, and by many others hyposulfurous acid. The first of these names is conventional and without theoretical significance; the second, although recommended by the Nomenclature Committee of the American and London Chemical Societies (see Crane and Patterson "Literature of Chemistry," p. 180), is distinctly irrational, since logically the name hyposulfurous acid should be applied (as it sometimes is) to the acid H_2SO_2 (of which derivatives only have been prepared). This last acid is, however, commonly called sulfoxylic acid. The confusion could be avoided and a rational system of nomenclature for these sulfur acids introduced by giving the acid H_2SO_2 its logical name, hyposulfurous acid, and giving the disulfur acid $H_2S_2O_4$ the new name dithionous acid, which would indicate that it stands in the same relation to sulfurous acid (and hyposulfurous acid) as dithionic acid stands to sulfuric acid (and sulfurous acid). These series of sulfur acids would then be: H_2SO_2, hyposulfurous; $H_2S_2O_4$, dithionous; H_2SO_3, sulfurous; $H_2S_2O_6$, dithionic; H_2SO_4, sulfuric. In the interest of the introduction of this rational nomenclature, the names "dithionous acid" and "dithionite" are used throughout this article.

This paper is a further contribution to the interpretation of this potential of sulfur dioxide, and of its behavior as an oxidizing and reducing agent. The experiments refer chiefly to the potentials exhibited at a platinized platinum electrode by a half-cell with various concentrations of sulfite and hydrogen ion in the presence of various other substances, and under different conditions of agitation and temperature. This half-cell was measured in combination with a hydrogen half-cell in which nearly the same hydrogen-ion concentration prevailed.

This investigation was assisted financially by a grant from the Carnegie Institution of Washington.

II. Hypotheses as to the Electrode Process in the Sulfite Half-Cell and the Thermodynamic Relations Involved

In order to facilitate the appreciation of the somewhat complex effects to be described in the following sections of this article, there may be presented in advance the following hypotheses, of whose adequacy to explain the phenomena the reader can judge as these are described. To the chemical equations numerical values are appended which show the free-energy decreases[3] attending the reactions at 25° when all the ions involved have a concentration of 1 molal.

1. The potential produced when a platinum electrode is placed in a solution of sulfurous acid arises from the tendency of this acid to reduce to a lower oxidation state, not from its tendency to oxidize to sulfuric acid in accordance with the electrode reactions

$$HSO_3^- + H20 = SO_4^{--} + 3H^+ + 2E- - 4245 \text{ cal. or} \qquad (1)$$
$$SO_2(g) + 2H_2O = SO_4^{--} + 4H^+ + 2E- - 6545 \text{ cal.} \qquad (2)$$

If the potential were determined by these reactions, the expressions for it would be

$$E = -0.092 - 0.0296 \log \frac{(SO_4^{--})(H^+)^3}{(HSO_3^-)} = -0.142 - 0.0296 \log \frac{(SO_4^{--})(H^+)^4}{p_{SO_2}} \qquad (3)$$

2. The sulfurous acid undergoes slight spontaneous decomposition into

---

[3] These free-energy decreases were calculated from the following data: $1H_2O$ (1), −56,560 cal.; $1HSO_3^-$ (1m.), −123,920 cal.; $1SO_2$ (1 atm.), −69,660 cal.; $1SO_4^{--}$ (1m.), −176,235 cal.; $1S_2O_3^{--}$ (1 m.), −121,345 cal.; $1S_2O_4^{--}$ (1 m.), −134,305 cal. The first three values are those given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 607. That for $1SO_4^{--}$ was obtained by Sherrill and Noyes, THIS JOURNAL, 48, 1871 (1926), through revision of the value computed by Lewis and Randall. The free energy of $1S_2O_3^{--}$ at 25" was computed from that of $1HSO_3^{--}$ and from the equilibrium constant 0.013 at 11° determined by Foerster and Vogel, *Z anorg. allgem. Chem.*, 155, 189 (1926), for the reaction $HSO_3^- + S(s) = H^+ + S_2O_3^{--}$, neglecting the difference in temperature. That for $1S_2O_4^{--}$ was derived from the reduction potential (+0.009 volt) which was determined electrometrically by Jellinek, *Z. Electrochem.*, 17, 163 (1911), for the electrode reaction $S_2O_4^{--} + 2H_2O = 2HSO_3^- + 2H^+ + 2E-$, assuming the acid $H_2S_2O_4$ to be completely ionized, as the other disulfur acids $H_2S_2O_3$ and $H_2S_2O_6$ appear to be.

sulfuric acid and a lower reduction product, namely, dithionous acid $H_2S_2O_4$, in accordance with the reaction

$$3HSO_3^- = SO_4^{--} + S_2O_4^{--} + H^{\cdot} + H_2O - 4660 \text{ cal.} \qquad (4)$$

3. The sulfurous acid and the so produced dithionous acid are (as concluded by Carter and James) the electromotively active substances to which the electrode quickly responds and of which the concentrations determine its potential, so that the actual electrode reaction is

$$S_2O_4^{--} + 2H_2O = 2H^{\cdot} + 2HSO_3^- + 2E^- + 415 \text{ cal. or} \qquad (5)$$

$$S_2O_4^{--} = 2SO_2(g) + 2E^- + 5015 \text{ cal.} \qquad (6)$$

The corresponding expression for the electrode potential is

$$E = +0.009 - 0.0296 \log \frac{(HSO_3^-)^2(H^+)^2}{(S_2O_4^{--})} = +0.109 - 0.0296 \log \frac{(p_{SO_2})^2}{(S_2O_4^{--})} \qquad (7)$$

4. The dithionous acid itself gradually decomposes in solutions of large hydrogen-ion concentration according to the equation

$$2S_2O_4^{--} + H^{\cdot} + H_2O = S(s) + 3HSO_3^- + 46{,}590 \text{ cal.} \qquad (8)$$

or, more strictly, since sulfur rapidly unites with sulfurous acid to form thiosulfuric acid until this attains a considerable concentration, the dithionous acid decomposes in accordance with the equation

$$2S_2O_4^{--} + H_2O = S_2O_3^{--} + 2HSO_3^- + 44{,}015 \text{ cal.} \qquad (9)$$

5. The above-given free-energy values show that Reactions 4, 8 and 9 tend to take place in the direction in which they are written (when the other ion concentrations are 1 molal) in case the $S_2O_4^{--}$ concentration has the following values

Reaction 4, when it is less than 0.0004 molal.
Reaction 8, when it is greater than 10^{-17} molal.
Reaction 9, when it is greater than 10^{-16} molal.

These conditions are probably fulfilled under the actual conditions, as shown at the end of Section VII.

6. A fairly definite concentration of dithionite ion and a fairly definite potential establish themselves as a result of a steady state in which the quantity of this ion being produced by Reaction 4 is equal to that being destroyed by Reaction 9. Certain plausible mechanisms can be formulated from which a steady state would result, but they are so hypothetical that they will not be reproduced here.

7. The possibility should also be considered that sulfur, not dithionous acid, is the reduction product which in association with sulfurous acid determines the electrode potential; for sulfur could be produced by the decomposition of sulfurous acid, as a result of the successive occurrence of Reactions 4 and 8, in accordance with the equation

$$3HSO_3^- = S(s) + 2SO_4^{--} + H^+ + H_2O + 37{,}270 \text{ cal.} \qquad (10)$$

Indeed, not only is this reaction thermodynamically possible, but spontaneous decomposition of solutions of sulfurous acid into sulfur and sulfate has been observed at 100–180° by many investigators.[4] The sulfur so produced would, however, be expected to determine the electrode potential in the case, and only in the case, that Reaction 8 takes place so rapidly that its equilibrium conditions are substantially maintained. In that case the electrode potential would have a definite value corresponding to the electrode reaction

$$S(s) + 3H_2O = HSO_3^- + 5H^+ + 4E^- - 45{,}760 \text{ cal. or} \quad (11)$$

$$S(s) + 2H_2O = SO_2(g) + 4H^+ + 4E^- - 43{,}460 \text{ cal.} \quad (12)$$

Hence

$$E = -0.496 - 0.0296 \log (HSO_3^-)^{1/2}(H^+)^{5/2} = -0.471 - 0.0296 \log (p_{SO_2})^{1/2}(H^+)^2 \quad (13)$$

It has, however, already been stated that James and Carter concluded that sulfur was not the active reduction product, and confirmation of this conclusion is afforded by the measurements presented in this paper.

III. Solutions, Apparatus and Experimental Procedure

In the earlier experiments the electrode vessel could not be conveniently agitated, and the sulfur dioxide was introduced in solution. This plan was employed only in the experiments with the half-cell containing sulfite and dithionate, and in those upon the effect of the initial condition of the electrode. In all the later work sulfur dioxide gas was introduced into the cell and maintained at the desired partial pressure by bubbling through the cell a known mixture of this gas with nitrogen or other diluent. This gave better control and furnished a convenient means of agitation.

In the earlier procedure air-free sulfurous acid solution was prepared by bubbling sulfur dioxide, generated by displacement from sodium bisulfite, through boiled distilled water kept under nitrogen. Dithionic acid was made from a solution of the pure barium salt (prepared for us by Mr. R. D. Pomeroy) by adding the equivalent amount of sulfuric acid and filtering off the precipitated barium sulfate. This solution was also kept under nitrogen. By a simple arrangement the solutions could be admitted to nitrogen-filled burets without exposing them to the air at any time. The burets were then used for analyzing the solutions and for filling the cell. This was done by extending the buret tips through the stopper of a nitrogen-filled mixing vessel into which the desired amounts of solution were run and mixed by shaking. The mixing vessel communicated with the electrode chamber, which had been swept out with nitrogen. Both acids were analyzed prior to use, but the sulfite concentration in the cell solution was always determined after taking down the cell, since an error might otherwise result due to the appreciable vapor pressure of the sulfur dioxide.

The potential measurements in all of the work were made by means of a Type K Leeds and Northrup potentiometer. The sulfite half-cell was joined through a stopcock with a hydrogen half-cell containing sulfuric or hydrochloric acid. It was especially important to keep the two solutions separated, for the presence of a small

---

[4] See Foerster, Lange, Drossbach and Seidel, *Z. anorg. allgem. Chem.*, 128, 245 (1923), who in an account of their own extensive research on this subject include a bibliography of previous work. See also Jungfleisch and Brunel. *Compt. rend.*, 156, 1719 (1913), and Bassett and Durrant, *J. Chem. Soc.*, 131, 1401 (1927), who regard dithionous acid as the intermediate product; also K. Jellinek and E. Jellinek, *Z. physik. Chem.*, 93, 325 (1919), who showed that dithionite decomposes in accordance with Reaction 8.

amount of sulfite poisoned the hydrogen electrodes. Each half-cell was equipped with two platinum foil electrodes, one centimeter square, sealed into glass stoppers placed about one centimeter apart and completely immersed in the cell solution. All electrodes were platinized (unless otherwise stated), those in the sulfite half-cell being replatinized for each set-up. Fig. 1 is a diagram of the hydrogen half-cell as it was used in all experiments. This was of a type used in former investigations in this Laboratory.[5] The side vessel is a saturator which was filled with some of the cell solution. The entering gas bubbled up through the helix, entered the bottom of the electrode vessel and passed out through the side trap. The hydrogen electrodes were considered to be operating satisfactorily when the difference of potential between them was not more than 0.1 millivolt and was not fluctuating; but this difference was usually less than 0.02 millivolt. The sulfite half-cell equipped for gas bubbling, which was used in the later work, was a duplicate of the hydrogen half-cell. The cell was kept in an oil thermostat.

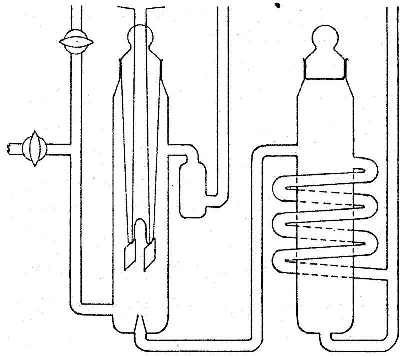


Fig. 1.—Hydrogen half-cell.

The apparatus for mixing the gases is shown diagrammatically in Fig. 2. Nitrogen was the diluent in most of the experiments. The gas from a cylinder was first purified from oxygen by bubbling it through two towers filled with copper turnings immersed in a mixture of equal volumes of concentrated ammonium hydroxide and saturated ammonium chloride solution. From these towers it passed through two wash bottles containing diluted and concentrated sulfuric acid to remove ammonia and water vapor. It passed through the capillary of a flow meter and was mixed with the current of sulfur dioxide. The sulfur dioxide was admitted from a gas cylinder, dried with concentrated sulfuric acid but not otherwise purified,[6] and passed through a flow meter. After the two streams joined, thorough mixing was insured by passing

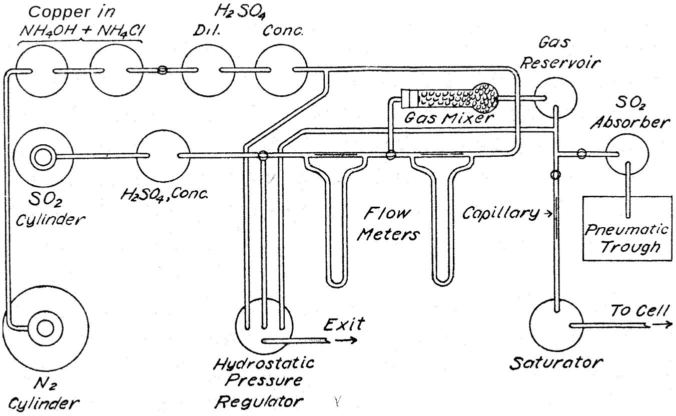


Fig. 2.—Apparatus for gas control.

---

[5] Schuhmann, This Journal, 46, 52 (1924).

[6] See L. Moser, *Z. anorg. allgem. Chem.*, *110*, 141 (1920).

the gas through a vessel filled with glass beads. The gas was then admitted to a small reservoir, passed thence to a saturator filled with the cell solution and finally led into the saturator which comprised part of the cell. The flow of gas was kept constant by means of by-passes to hydrostatic pressure exits arranged as shown in the figure and consisting of tubes whose depth of immersion in a well of transil oil could be varied. Gas was kept bubbling from them so that constant pressures were maintained. Nujol was used in the flow meters and their sensitivity was increased by inclining the gages. The various parts of the apparatus were joined with rubber tubing.

The gas mixtures corresponding to the gage settings adopted were analyzed by passing them slowly into an absorption vessel filled with standard iodine solution (to remove the sulfur dioxide) and then into a pneumatic trough, where the nitrogen was collected over water. The excess of iodine was titrated with thiosulfate solution. The agreement of the analyses is shown by the following data: for one gage setting the mixtures were found to contain 7.23, 7.29 and 7.32% of SO_2; for another setting, 23.8, 24.1 and 24.1% of SO_2.

IV. Behavior of a Platinum Electrode in Sulfurous Acid Solutions

When a half-cell that consists of a platinized electrode in an air-free solution of sulfurous acid containing also some stronger acid is allowed to stand at 25° for some hours without bubbling or other agitation, there is established a tolerably constant and reproducible potential, namely, one which as a rule changes by less than two centivolts during several days. This potential has a value of about -0.37 volt, referred to that of the molal hydrogen electrode as zero. If now a mixture of nitrogen and sulfur dioxide (at a partial pressure equal to its vapor pressure in the solution) is bubbled steadily through the solution, so as to mix the liquid surrounding the electrode with the rest of the solution, the potential immediately increases in negative value—an increase which in the course of half an hour usually amounts to two to four centivolts. It then reverts to less negative values, rapidly during the first two hours and then more slowly, attaining after some five or six hours a fairly constant value which may be one or two centivolts more negative than that exhibited before the solution was agitated. When the bubbling is stopped, the potential attains within twenty minutes substantially the value which it had previous to the agitation. If after standing for several hours the bubbling is resumed, the same sequence of phenomena is observed. Thus after a few hours of bubbling the same fairly constant value is obtained as before, usually differing from it by only two or three millivolts; and on quiet standing nearly the same final value results as before. The two duplicate electrodes in the cell then usually check within one or two millivolts, though occasionally they differ by as much as five or six millivolts. The constancy and reproducibility of the electrodes under quiet conditions are shown in detail by the data in Tables III and IV considered below.

The behavior just described is illustrated by Fig. 3, in which graphs for typical half-cells are drawn by plotting as ordinates the potential of the whole cell (with a hydrogen electrode in its other half-cell) and as abscissas the elapsed time in hours. Broken lines are used to indicate periods during which gas was bubbling through the cell; solid lines, periods when there was no agitation.

It will be seen from Fig. **3** and the above statements that four different effects are to be accounted for: (1) production under quiet conditions of a fairly reproducible potential of about **–0.37** volt; (2) production by short agitation of the solution of a much more negative potential varying much with the conditions, thus one of about **–0.410** and –0.393 in the cells considered; **(3)** production by long agitation of a potential steadily decreasing in negative value and slowly approaching a value not much larger than that in the quiet state; thus in the two cells after nine to thirteen hours' bubbling the values were **–0.370** and **–0.373**; **(4)** reestablishment of the original quiet-state value when the agitation is stopped, and reproduction of a much higher negative value when the stirring is resumed.

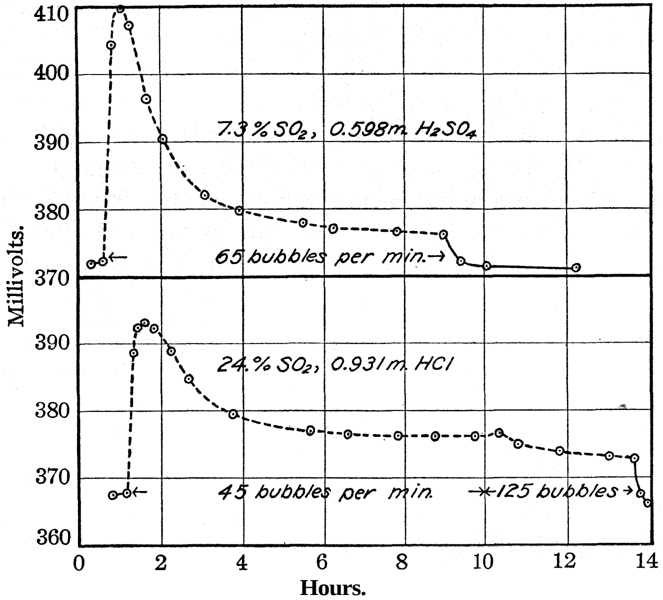


Fig. 3.—Effect of agitation of the sulfite solution upon the electromotive force.

We are not able to present evidence for specific explanations of these agitation phenomena, but they seem to be due to a combination of catalytic and adsorption effects at the electrode, which give rise at its surface to concentration changes that are distributed by stirring the solution.

V. Effect of Preliminary Treatments of the Sulfite Electrode

The following experiments were made in order to establish more fully the conclusion that the potential arises from sulfurous acid and a decomposition product and not from some accidental initial condition of the electrode. One series of experiments was made in which the electrode was treated in various ways before it was placed in the solution; another was made in which a small current was passed through the half-cell in one direction or the other, whereby the electrode would be charged with hydrogen or oxygen gas.

The first series was made with a half-cell with platinum electrodes in a mixture of 0.037–0.046 N sulfurous acid and 0.047 N dithionic acid, which will later be shown to have no specific effect on the potential, the other half-cell containing sulfuric acid (at 0.078–0.081 N) of about the same hydrogen-ion activity. The electromotive force of these cells after successive intervals of quiet standing is shown in Table I. In Expt. 1 platinized electrodes were used but in the other experiments the electrodes were deplatinized. In Expts. 1 and 2 the electrodes were charged with hydrogen by electrolysis in a sulfuric acid solution and then immediately put into the cell. In Expts. 3 and 4 they were allowed to stand overnight in concentrated sulfurous acid solution and in dithionic acid solution, respectively.

TABLE I

EFFECT OF VARIOUS INITIAL TREATMENTS OF THE ELECTRODE ON ITS POTENTIAL

Expt. no.	Electrode initially treated with	Electromotive force in millivolts after 10–20 min.	1 day	Several days
1	Hydrogen	...	415	447
2	Hydrogen	...	513	477
3	H_2SO_3	475	465	...
4	$H_2S_2O_6$	459	454	...

In a second series of experiments a current was passed through the cell, making the sulfite electrode in some cases the anode and in others the cathode. Somewhat similar experiments had already been made by Carter and James.' Our experiments were all made with a half-cell con-

TABLE II

ELECTROMOTIVE FORCE OF THE CELL AFTER POLARIZATION

Expt. no.	Sulfite electrode made	Applied potential Volts	Minutes	Before polarization	Electromotive force at various times after polarization 1–2 min.	5 min.	10 min.	20 min.	1 hr.	2 hrs.	1 day
5	Cathode	0[a]	5	434	304	340	400	435	439	434	...
6	Cathode	0"	5	427	314	344	389	432	441	433	429
7	Anode	1.6	3	427	484	465	455	449	438	...	427
8	Cathode	65[b]	3	433	250	...	...	444	456	460	460
9	Cathode	65[b]	20	460	220	...	275	305	327[c]	333	435[d]
10	Anode	65[b]	20	425	...	585	530	495	468	461	453

[a] In these cases the cell circuit was closed but no external voltage was applied.

[b] The resulting current was 0.01 ampere.

[c] Thirty minutes after polarization, when the electromotive force was about 340 mv., the cell was shaken; this stopped the rise of the electromotive force for a time.

[d] After two days.

taining platinized electrodes in a mixture containing sulfurous acid at 0.043 N (corresponding to a sulfur dioxide pressure of 0.014 atm.) and sulfuric acid at 0.068 *N;* the other half-cell with the hydrogen half-cell contained sulfuric acid at 0.081 *N*, which has about the same hydrogen-ion activity as the mixture of the two acids. The results are shown in Table II.

It will be seen that although the polarization produced great differences in the initial values of the electromotive force, all the final values are of about the same magnitude (430460 millivolts).

These two series of experiments clearly show that a platinum electrode in sulfurous acid solutions establishes a fairly reproducible potential which is independent of variations in the initial condition of the electrode.

VI. Sulfite Half-Cells with Dithionic Acid

It had been shown by previous investigators that the potential observed with solutions of sulfurous and sulfuric acids is not much affected by the concentration of sulfate ion, showing that this ion is not electromotively active. It was thought possible, however, that the intermediate oxidation product, dithionic acid ($H_2S_2O_6$), might establish with sulfurous acid a definite potential. Cells were, therefore, set up in which the electromotive force observed when sulfurous acid was present with dithionic acid could be compared with that produced when the latter acid was replaced by sulfuric acid. The results are shown in Table III. All potentials are expressed in millivolts.

Since it took several hours or more for the duplicate electrodes in the sulfite half-cell to come to such equilibrium as to check each other well, values were usually not recorded until the following day after starting a run; after this the duplicate electrodes almost always checked to within one or two millivolts.

Table III

Electromotive Force at 25° of Cells with Sulfurous, Sulfuric and Dithionic Acids

	Sulfite half-cell					Hydrogen half-cell		
Expt. no.	Normality of H_2SO_3	Normality of H_2SO_4	Normality of $H_2S_2O_6$	Press. of SO_2, atm.	Molal activity of H^+	Normality of H_2SO_4	Molal activity of H^+	Calcd. potential
1	0.043	0.068	None	0.014	0.045	0.081	0.047	79
2	.046	None	0.047	.015	.044	.081	.047	79
3	.057	0.019	.016	.017	.032	.050	.031	89

Same Experiments Continued

Expt. no.	Electromotive force of cell after successive days 1	2	3	4	7	9	Potential of sulfite half-cell
1	428	433	433	...	...	...	−354
2	415	...	...	447	449	...	−370
3	479	474	470	470	466	459	−370

In calculating the potential of the sulfite half-cell no allowance was made for liquid potential; for the acid used in the hydrogen half-cell was of a strength calculated to have about the same hydrogen-ion activity as that of the mixture in the other half-cell. Hydrogen-ion activities were calculated with the aid of the data published by Sherrill and Noyes.[7] In estimating the ionic strength the dithionic acid was considered to be completely dissociated. Conductivity data show it to be a very strong acid.[8] Equilibrium pressures of sulfur dioxide were calculated by Henry's law, correction being made for the dissociation of the sulfurous acid.

It will be seen that the potential is not much different whether the acid present with the sulfurous acid is sulfuric or dithionic, showing that the electrode process which determines the potential does not directly involve either of these acids.

To establish completely the conclusion that the potential is not dependent upon these oxidation products of sulfurous acid, a series of cells was set up in which sulfur dioxide was the only sulfur compound added and the desired acidity was produced by hydrochloric acid. In this work sulfur dioxide gas diluted with nitrogen was bubbled through the cell, to establish a definite activity of sulfurous acid and to provide efficient stirring; the electromotive force was read, however, only after a long period of quiet standing. In order that the comparison might be direct, a similar series was made in which sulfuric acid was again used. The results which are presented later (in Table IV) show that, provided the hydrogen-ion concentration is nearly the same, hydrochloric acid and sulfuric acid produce (in association with sulfurous acid) substantially the same electromotive force.

VII. The Potential of Sulfite Half-Cells and the Effect upon it of the Concentration of Sulfurous Acid and of Hydrogen Ion

The series of comparative experiments with hydrochloric and sulfuric acids (referred to in Section VI), in which a definite concentration of sulfurous acid was attained by bubbling sulfur dioxide diluted with nitrogen through the cell and measuring the electromotive force after periods of quiet standing, also served to determine to what extent the potential depends upon the activity of sulfurous acid and upon that of hydrogen ion. A pair of comparative experiments at 25 and 50° was also made to determine the effect of temperature.

The results are presented in Table IV. The electromotive forces are those of cells of the type Pt + H_2 (1 atm.), HCl or H_2SO_4 (with H^+ at c_H), $\{SO_2$ (at p) + HCl or H_2SO_4 (with H^+ at $c_H)\}$, Pt. The electromotive forces and separate potentials are all expressed in millivolts. The recorded values

---

[7] Sherrill and Noyes, THIS JOURNAL, 48, 1861 (1926).

[8] See Abegg's "Handbuch der anorganischen Chemie," IV, 1, 539 (1926).

of the electromotive force of the cell are the daily averages of readings taken at intervals of one, two or three hours throughout the day during which the sulfur dioxide was not bubbling through. An asterisk indicates that after taking the reading the gas mixture was bubbled for several hours through the cell, which was then allowed to stand quietly overnight.[9]

TABLE IV

ELECTROMOTIVE FORCE OF CELLS WITH SULFUROUS, SULFURIC AND HYDROCHLORIC ACIDS

		Sulfite half-cell			Hydrogen half-cell		
		Molality					
Expt. no.	Temp., °C.	H_2SO_4	HCl	SO_2 in gas, %	Molal acid	Activity of H^+	Potential calcd.
1	25	0.598	0.0	1.5	0.598	0.599	13
2	25	.598	.0	7.3	.598	.599	13
3	25	.598	.0	24.0	.598	.599	13
4	25	.0	.931	7.3	.931	.955	1
5	25	.0	.931	24.0	.931	.955	1
6	25	.0	.931	100.0	.931	.955	1
7	25	.0	.205	7.3	.205	.170	46
8	50	.0	.931	7.3	.931	.955	1

	Electromotive force of whole cell after successive days as follows								
Expt. no.	1 8	2 9	3 10	4 11	5 12	6 13	7 14	Best value	Sulfite half-cell potential
1	468.1*	...	394.5*	389.2*	384.1*	381.1*	384.5	...	...
	395.0	...	393.0*	393.0	379.4	377.6*	374.6	...	...
2	372.2*	371.7*	372.2*	372.3	377.5	...	378.9	372	−359
	377.5*	371.3	...	...	...	...	...		
3	370.7*	369.1	...	...	...	...	382.6*	370	−357
	370.5*	369.1	370.6	...	...	...	...		
4	368.2*	370.5	370.7*	370.9	370.5	370.2*	369.4	370	−369
5	367.5*	366.5*	366.4	366.8	...	...	366.4	366	−365
6	364.7*	...	...	...	...	...	...	365	−364
7	436.5*	425.6*	...	396.5*	389.8*	390.4*	388.0*	386	−340
	388.2*	385.5*	...	386.0*	385.5*	386.3*	386.4*		
	392.2*	387.8*	381.4	382.3	381.0	...	...		
8	360.4*	357.6*	357.4	355.1*	363.7*	374.7	372.5*	358	−357

---

[9] In cases where an experiment consisted merely in increasing the pressure of sulfur dioxide, the initial value recorded is that obtained on the first or second day after making such an increase, when it was believed that the equilibrium concentration had been established. In experiments which were the first of a series, where the air had to be displaced from the cell and the sulfurous acid concentration built up from an initial value of zero, the first recorded figures are in most cases those obtained after several days of gas bubbling, during which time the negative potential was decreasing from that corresponding roughly to an oxygen electrode; for although the electrodes were initially charged with hydrogen, the initial conditions in the cell were such as to establish a highly negative potential. Bubbling was not continued overnight, as it was not desirable to allow the gas to flow so long without observation. Prior to Expts. 1 and 4 the air in the cell was displaced with nitrogen before any sulfur dioxide was admitted. In the other independent experiments the gaseous mixture was started through at once. In Expt. 7 the third row of readings were those after 15, 16, 17, 18 and 19 days.

The hydrogen-ion activity of the hydrogen half-cell and its corresponding potential were calculated from the data given by Lewis and Randall[10] in the cases where hydrochloric acid was used, and from the data of Noyes and Stewart[11] where sulfuric acid was employed. The potential of the sulfite half-cell was obtained by subtracting the calculated value of that of the hydrogen half-cell from the "best value" of the electromotive force of the whole cell, no allowance being made for the liquid potential, which must have been small, since the hydrogen-ion concentrations had been made approximately equal.

Before considering the effects of concentration, it may be pointed out that the results confirm the previous statement that about the same electromotive force is produced with hydrochloric as with sulfuric acid, since the values of the potential obtained with the latter fit in with those obtained with hydrochloric acid both at higher and lower hydrogen-ion activities. There can therefore be no doubt that sulfuric acid is not electromotively active in establishing the potential.

Coming now to concentration effects, it is seen from Expts. 2 and 3 or from Expts. 4–6 that increasing 3.3-fold, or even 14-fold, the partial pressure of the sulfur dioxide has little, if any, effect upon the value of the potential.

It will also be seen that decrease in the hydrogen-ion activity produces a less negative value of the potential. Thus from Expts. 4 and 7 it is seen that a 5.6-fold decrease (from 0.955 to 0.170 molal) causes a decrease of 29 mv., while $^1/_2$ (H^+) per faraday would require a decrease of 22 mv. To express the observed results, the function of (H^+) which occurs in that electrode potential equation should therefore be $(H^+)^{4/3}$.

It is also important to note the absolute value of the potential of the sulfite half-cell. It will be seen that its mean value of 25° at a hydrogen-ion activity of 0.96 N is —366 mv., or —0.37 volt within the error of the measurements. The experimental values of the sulfite potential are therefore expressed by the empirical equation

$$E = -0.37 - 0.0296 \log(H^+)^{4/3} \qquad (14)$$

The effect of temperature is shown by Expts. 4 and 8, which were made at 25 and 50°, respectively. The best value of the potential is seen to be only 12 mv. less negative at 50 than at 25°. This shows that the same electrode process is involved at both temperatures, and confirms the conclusion that the potential is not an accidental one. The small change observed, based as it is on one experiment, should not be considered to indicate even the direction of the effect of temperature.

Regarding this —0.37 volt as a sulfite–dithionite potential, it shows,

---

[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923,** p. **336.**

[11] Noyes and Stewart, THIS JOURNAL, 48, **1870** (1926).

when considered in relation to the molal potential +0.009 of that combination as expressed by Equation 7, that the $S_2O_4^{--}$ concentration in the assumed steady state, when (H^+) and (HSO_3^-) are 1 molal, is only $10^{-12.8}$ molal. Even this minute concentration is, however, about 20,000 times larger than the $S_2O_4^{--}$ concentration ($10^{-17.1}$ molal) that is shown by Equation 8 to be in equilibrium with solid sulfur and sulfurous acid when (H^+) and (HSO_3^-) are 1 molal.

VIII. Half-Cells with Sulfurous Acid and Sulfur

The experiments described in Sections VI and VII clearly showed that neither the usual oxidation product of sulfur dioxide, sulfuric acid, nor the intermediate oxidation product, dithionic acid, is electromotively active in association with sulfurous acid. Yet it has been seen that the potential set up in a solution of sulfurous acid is a characteristic, not an accidental, one. Attention must therefore be directed toward its reduction products.

A natural reduction product to consider is solid sulfur—a possibility which was suggested in Section II. If it were the electromotively active substance, the electrode potential established would be that corresponding to Equation.13 This requires an increase of 15 mv. in the negative value of the potential for a ten-fold increase in the pressure of the sulfur dioxide, and an increase of 59 mv. for a ten-fold increase in hydrogen-ion activity. The results of Table IV showed that in fact variation of the pressure of the sulfur dioxde has little or no effect, and that increase in hydrogen-ion activity has only about two-thirds of the required effect. Although these results with sulfur dioxide are not divergent enough to prove that sulfur is not the active substance involved in the electrode process, yet the absolute value of the molal electrode potential is hardly reconcilable with this assumption, for the observed value is only −370 mv., while that calculated from the free-energy data by Equation 13 is −471 mv. Thus there is a difference of 100 mv., which is about ten times as great as the variation in constancy and reproducibility shown by the data when the conditions are those of strong acidity and moderate pressure of sulfur dioxide. This shows that much more strongly reducing conditions prevail than would be caused by solid sulfur, and therefore that dithionite (or some other strongly reducing substance) is present at higher concentration than that which is in equilibrium with sulfur and sulfurous acid according to Equation 8.

Nevertheless, it seemed worth while to test further the possibility that sulfur is the active substance by depositing it in finely divided form on the electrode. The presence of this added sulfur should give a more constant and reproducible potential and one more nearly of the calculated magnitude if this substance is really electromotively active.

These experiments were first carried out at 50° with Cell 8 of Table IV after taking the readings there recorded. At 50° a cell of this composition should have an electromotive force of approximately 430 mv. if sulfur and sulfur dioxide are the electromotively active substances. The free-energy decrease that attends Reaction 12 at 50° is calculated from that at 25° and from the heat-content decrease at 37.5° (–67,400 cal.) to be —41,460 cal., and the corresponding electrode potential equation is

$$E = -0.449 - 0.0321 \log p_{SO_2}{}^{1/2}(H^+)^2 \qquad (15)$$

The two electrodes in the sulfite cell were removed and one of them was given a shaggy coating of free sulfur by electrolysis in a solution of sodium polysulfide. They were then soaked in hot water for a couple of hours, rinsed thoroughly and returned to the cell. The gas mixture was bubbled through the half-cell for several hours on the first and second days, after which the contents were no longer agitated. After standing overnight the electromotive force returned approximately to that (358 mv.) shown before the sulfur treatment, the two electrodes checking within 2 mv.; but during the next five days it gradually became more negative, after which it showed no consistent trend, though subject to daily fluctuations of 5–6 mv. It showed an average value of 412 mv. at the sulfur-treated electrode, and of 425 mv. at the other electrode.

The electrodes were again removed, cleaned and replatinized. One of them was coated with a thick, sirupy solution of sodium polysulfide and sulfur was precipitated from it by fuming it with concentrated hydrochloric acid overnight. The electrodes were then subjected to a very thorough washing and leaching with warm water; they were returned to the cell and gas was bubbled through it to replace any air. After standing quietly overnight the electromotive force of the cell was 396 mv. at the sulfur-treated electrode and 410 mv. at the other. The values rose over a period of six days, and then remained constant within 3 mv. for four days more at 444 mv. and 440 mv., respectively. These values are seen to be approximately equal to the calculated value (430 mv.), and indicate that at 50" the presence of sulfur on or near the electrode tends to establish the potential required by electrode Reaction 12 involving sulfur and sulfur dioxide.

In view of these results it seemed desirable to investigate the effect of the addition of sulfur at 25° also. The results so obtained are shown in Table V. One electrode was untreated but the other was coated with sulfur by the second method above described, and after the reading first recorded in the table some powdered rhombic sulfur was added to the sulfite half-cell.

It will be seen that the values obtained at 25° with the uncoated electrode are apparently not changed by adding solid sulfur to the solution,

TABLE V

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SOLID SULFUR ADDED

HCl in each half-cell, 0.829 *M*; H^+ activity, 0.804 *M*; calculated potential of hydrogen half-cell, +6 mv.

Sulfite half-cell Electrode sulfur treated	% SO_2 in dry gas	Electromotive force of cell after successive days as follows								*Best* value	Potential of sulfite half-cell
		1	2	4	5	6	8	9	11		
No	7.3	380.0"	374.0"	372.9"	375.6	375.5	375.5"	375.2	376.9	375	−369
Yes	7.3	396.0"	387.5"	375.2"	390.6	387.9	389.0"	376.0	377.9	385	−379
No	24.0	373.4"	373.3	...	...	...	...	...	...	373	−367
Yes	24.0	380.6"	379.4	...	...	...	...	...	...	380	−374

[a] After this reading the gas mixture was bubbled for several hours through the cell, which then stood quietly overnight.

and even the values obtained at the sulfur-treated electrode differ from those at the untreated electrode by only 10 mv. in many cases, and show no tendency to deviate more than this.

These facts show that at 25° the additional sulfur does not determine the potential of the half-cell and that sulfur would have little effect even if it were formed on the electrode through decomposition of the sulfurous acid in cases where sulfur was not added. This presumably arises from the facts that it has much less electromotive activity than dithionite, and that the decomposition of the dithionite by Reaction 8 is not rapid enough, even though it may be catalyzed by solid sulfur, to reduce its concentration to that corresponding to the equilibrium conditions of Reaction 8. The result at 50° showing that the addition of sulfur causes the theoretical sulfur potential to be approximated is probably due to the fact that at this higher temperature the decomposition of the dithionite is rapid enough in the presence of sulfur to establish approximately the equilibrium conditions of Reaction 8.

IX. Sulfite Half-Cells in the Presence of Oxygen

An extensive investigation was carried out some years ago by Edgar, and reported later by Lewis, Randall and Bichowsky,[12] in which sulfur dioxide diluted with air was bubbled through a half-cell containing sulfuric acid solution and an iridized platinum electrode. The electrode potential of this half-cell was measured against a half-cell having a mercury–mercurous sulfate electrode and containing sulfuric acid at a concentration equal to that in the sulfite half-cell. Reproducibility to within about 1 mv. was obtained.

The electromotive forces directly observed by Edgar were calculated by us over to the molal hydrogen electrode with the aid of the values of Randall and Cushman[13] for the cell H_2 (1 atm.), H_2SO_4, $Hg_2SO_4(s) + Hg$, so as to obtain the electromotive forces of the cell H_2 (1 atm.), H_2SO_4 (c),

---

[12] Lewis, Randall and Bichowsky, THIS JOURNAL, 40, 360 (1918).

[13] Randall and Cushman, *ibid.*, 40, 393 (1918).

H_2SO_4 (c) + SO_2 (g). By subtracting from these the calculated values for the potential of the hydrogen half-cell, the potentials of the sulfite half-cell were obtained.

Table VI shows the results obtained by Edgar with the moderately concentrated solutions of sulfuric acid. The concentration of the sulfuric acid in the hydrogen half-cell was always the same as that in the sulfite half-cell. The potentials are as usual expressed in millivolts. The values in the last column were obtained from those in the preceding one by subtracting **0.0296** log p_{SO_2}. These values correspond to the assumption that the change in potential is determined by an electrode reaction including among the reduced substances $\frac{1}{2}SO_2$ per faraday. This fact was naturally interpreted by the earlier investigators as indicating that the observed quantity was a sulfite–sulfate potential established in accordance with Equation **3** of Section II.

TABLE VI

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SULFUR DIOXIDE AND AIR

(Calculated from Edgar's data)

Expt. no.	Sulfite half-cell Molality of H_2SO_4	 Pressure, SO_2 atm.	Hydrogen half-cell Activity H^+	 Potential calcd.	E.m.f. of cell	Sulfite half-cell Potential	 SO_2 at 1 atm.
1	0.5009	0.00689	0.497	18	458	−440	−376
2	.5009	.01328	.497	18	445	−427	−373
3	.5009	.02479	.497	18	437	−419	−372
4	.5009	.05080	.497	18	430	−412	−372
5	.5009	.1091	.497	18	422	−404	−376
6	.5125	.969	.508	17	371	−354	−354

The results shown by Table VI may be summed up as follows. When little or no oxygen is present, as in Expt. 6, the sulfite potential has the value −**354** mv., which corresponds closely to that (−358 mv.) required by our empirical Equation 14 of Section VII. But when, as in Expts. 1–5, oxygen is present and a considerable acid concentration prevails (this perhaps enabling the oxygen to cause oxidation) the potential is more negative (−**404** to −**440** mv.). This signifies that the reducing substance (the dithionite) involved in the steady state determining the potential is being destroyed not only by the spontaneous decomposition expressed by Equation **9** but also by oxidation by the air. Moreover, the negative value is increased by decreasing the concentration of the sulfite; that is to say, the potential becomes more oxidizing on diminishing the concentration of what is here regarded as the oxidizing substance. To explain this anomaly, one must assume that the concentration of the reducing substance (the dithionite) is decreased in still greater proportion when a lesser quantity of sulfurous acid is present from which it can be regenerated.

To study further the effect of oxygen, a series of experiments was made in which gas mixtures of air with sulfur dioxide were bubbled through a sulfite half-cell. The results are shown in Table VII.[14]

TABLE VII

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SULFUR DIOXIDE AND AIR

Expt. no.	Sulfite half-cell Molal. H_2SO_4	Sulfite half-cell SO_2 in gas, %	Hydrogen half-cell Activity of H^+	Hydrogen half-cell Potential, calcd.	Electromotive force of whole cell 1	2	3	4	8	6	7	Best value	Sulfite half-cell potential
1	0.590	1.5	0.594	13	512[a]	506[a]	491[a]	...	...	485[a]	491	489	-476
2	.590	7.3	.594	13	443	438[a]	437[a]	431	...	...	...	437	-424
3	.590	7.3	.594	13	498[a]	486[a]	490[a]	487[a]	477[a]	481[a]	477	483	-470
4	.590	24.0	.594	13	459[a]	453	425[a]	440[a]	435[a]	422	...	430	-417
5	.590	24.0[b]	.594	13	466[a]	465[a]	...	460[a]	470	...	...	465	-452

[a] After this reading the gas mixture was bubbled for several hours through the cell, which then stood quietly overnight before the nest reading was made.

[b] In this experiment the SO_2 was diluted with oxygen, instead of air.

It will be seen that the experiments presented in Table VII do not show the constancy or agreement with one another exhibited by those of Edgar. It is evident that our conditions, probably especially those prevailing at the sulfite electrode, were not nearly as favorable as those in Edgar's experiments. Our results are cited here, not to cast doubt upon the previous ones, but only to show how capricious the potential may be when the electrode process is complicated by the presence of oxygen.

X. The Oxidizing and Reducing Properties of Sulfurous Acid

Finally, reference should be made to the chemical behavior of sulfurous acid in relation to its electrode potential. An extensive series of researches on the oxidizing and reducing action of this substance has recently been carried out by Wardlaw, Carter and their associates.[15]

---

[14] The method of recording the data is the same as that in Table IV. Immediately following Expt. 1 the electrodes were removed and resaturated with hydrogen before being replaced. This appeared to produce a permanent decrease in the electromotive force of the cell, as was shown by the character of the bubbling curve and by the non-bubbling value obtained the following morning (455 mv.). The sulfur dioxide pressure was then changed to 7.3% in Expt. 2. Expts. 3, 4 and 5 form a new series in which a fresh solution was taken.

The air used in these experiments was drawn from the laboratory compressed air lines and was passed through a solution of sodium hydroxide and then through concentrated sulfuric acid. Oxygen was drawn from a gas cylinder and passed through the same solutions. After taking down the cells the solution was analyzed by first titrating with thiosulfate for sulfite content and then with sodium hydroxide for total acidity. The increase in the molality of the sulfuric acid was calculated to be about 0.004 mole, although this cell was in operation for twenty days.

[15] Wardlaw and Clews, *J. Chem. Soc.*, 117, 1093-1103 (1920); Wardlaw and Carter, *ibid.*, 1241-1247 (1920); Wardlaw and Pinkard, *ibid.*, 121, 210-221 (1922); Carter and Clews, *ibid.*, 125, 1880-1888 (1924); Carter and Lea, *ibid.*, 127, 499-510 (1925); Carter and Robinson, *ibid.*, 130, 1921-1923 (1927). For a summary of the results see Carter, *J. Soc. Chem. Ind.*, 45, 207-210 (1926); Wardlaw, *ibid.*, 45, 210-214 (1926).

These investigators have studied the effect at 95° or above of sulfurous acid, both as an oxidizing agent and as a reducing agent, on various combinations having a series of reduction potentials, namely, on different mixtures of ferrous and ferric chlorides, of ferrous and ferric phosphates, of cuprous and cupric chlorides, and of mercurous and mercuric chlorides, in the presence of the corresponding acid at widely varied concentrations. They have thus qualitatively determined the combinations which have near 95° such reduction potentials as cause them to be barely oxidized and such as cause them to be barely reduced by sulfurous acid at different acid concentrations. They have found in general: (1) that sulfurous acid, because of its tendency to undergo two entirely different reactions, behaves either as a reducing agent or an oxidizing agent depending on the nature of the combination acted upon and on the strength of the acid, (2) that at a given acid concentration the reduction potential of the combination acted upon need be varied by only a relatively small amount (say by 20 to 40 mv.) in order to change the action of sulfurous acid from a reducing one to an oxidizing one, and (3) that increase in acid concentration makes sulfurous acid a less powerful reducing agent, and also (to about the same extent) a more powerful oxidizing agent.

From a theoretical standpoint this chemical behavior of sulfurous acid may now be interpreted in the following way more quantitatively than was done by the English investigators.

Sulfur dioxide at 25° at 1 atm. in an aqueous solution containing hydrogen ion at 1 molal may be expected to behave toward other oxidation–reduction combinations of substances in three different ways according as the reduction potential of the latter (a) is more negative than -0.37 volt; (b) lies between -0.37 volt and -0.14 volt; (c) is more positive than -0.14 volt. (It may be recalled that the value -0.37 is the potential which sulfur dioxide has, under the specified conditions, with respect to its conversion into dithionite ion $S_2O_4^{--}$ as it exists in the steady reaction state, and that -0.14 is the potential which it has with respect to its conversion to sulfate ion, SO_4^{--}, at 1 molal.) For it is evident that sulfur dioxide may oxidize any combination with a reduction potential more reducing (less negative) than -0.37 volt, and that it may reduce any combination which has a potential more oxidizing (more negative) than -0.14 volt. Therefore it may either oxidize or reduce any combination with a potential between -0.37 and -0.14 volt, and which of these two possible effects actually occurs will depend on the relative rates of the oxidizing reaction and of the reducing reaction. For example, sulfur dioxide (at 25° and 1 atm. and with H^+ at 1 molal) can only reduce Fe^{++}(1 m.), Fe^{+++} (1 m.) for which E is -0.75 volt, or I^-(1 m.), I_2(s) for which E is -0.54 volt; and it can only oxidize Pb (s), Pb^{++} for which E is $+0.12$ volt, or H_2 (1 atm.), H^+ (1 m.), for which $E = \pm 0$. But it might either oxidize or reduce Hg (l) + Cl^-(1 m.), Hg_2Cl_2(s) for which E is —0.27 volt, or Cu(s), Cu^{++} (1m.) for which E is −0.34 volt. In fact, however, in such cases the oxidizing effect of sulfur dioxide (whereby it is converted to dithionite) seems to be more rapid than its reducing effect (whereby it is converted to sulfate), so that within the interval —0.37 to —0.14 volt it probably acts ordinarily as an oxidizing agent. If this is *the* case, the potential which a combination actually must have in order that it may be reduced by sulfur dioxide is —0.37, not —0.14, thus accounting for the condition mentioned in the Introduction that sulfur dioxide seems to be reducing through a narrower range than thermodynamic relations permit.

Increase of hydrogen-ion concentration, according to empirical Equation 14, extends the region (to more negative values than —0.37) within which sulfur dioxide can act oxidizing, and, according to theoretical Equation 3, it narrows the region (requiring more negative potentials than —0.14 in the combination acted upon) within which sulfur dioxide can act reducing. Thus increase of acidity should make sulfur dioxide more oxidizing, but less reducing, as the English investigators found.

XI. Summary

Experiments have been described in this article showing the electromotive force developed in various cells of the general type Pt, H_2SO_3 + HA at c_1, HA at c_2, H_2 + Pt, where c_1 and c_2 are so related that the hydrogen-ion concentration is nearly the same in the two solutions (thus largely eliminating the liquid potential), and where HA is sulfuric acid, dithionic acid or hydrochloric acid.

It is shown that fairly definite electromotive forces result when and only when the cells are allowed to stand quietly for many hours or for several days, since agitation immediately causes a large increase in the negative value of the electromotive force. This definite electromotive force is nearly independent of the concentration of the sulfurous acid and does not depend on whether the acid associated with it is sulfuric, dithionic or hydrochloric acid, thus proving that the anion of none of these acids determines the potential. At 25° the potential E of the sulfite half-cell (obtained by subtracting from the electromotive force the calculated potential of the hydrogen electrode) is approximately given by the empirical expression $E = -0.37 - 0.03 \log (H^+)^{4/3}$.

It is shown that the results are satisfactorily explained by the assumption, earlier made by Carter and James, that the sulfite potential arises from association with the sulfurous acid of one of its spontaneously produced reduction products, probably the acid $H_2S_2O_4$ (for which the rational name dithionous acid is proposed, in place of the conventional names hydrosulfurous or hyposulfurous acid used in the literature). It is suggested that the fairly definite potential is the result of a steady state in which the quantity of this acid produced per minute by the decomposition of sulfurous acid (into $H_2S_2O_4$ and H_2SO_4) becomes equal to the quantity of it destroyed per minute by its spontaneous decomposition (into H_2SO_3 and S or into $H_2S_2O_3$).

It is shown that the reduction product which determines the potential is not sulfur itself, for thermodynamic calculations require that the potential then be about 0.10 volt more negative than the observed value of —0.37 volt; moreover, experiments in which finely divided sulfur was added to the sulfite half-cell showed that it is not active enough to change the potential in the required direction. This is true at any rate at 25°, but there are indications that at higher temperatures, where the sulfur is more active and the rate of decomposition of the dithionous acid more rapid, sulfur may be the reduction product which determines the potential.

As an aid in the interpretation of the results the free energies and electrode potentials corresponding to all the sulfur reactions possibly involved have been derived from existing theremodynamic data and formulated (in Section II).

The existence of the definite steady-state potential (—0.37 volt at 25°) between sulfurous acid and its reduction product considered in connection with the thermodynamically known potential (—0.14 volt) of sulfite–sulfate, enables the behavior of this acid as an oxidizing agent and as a reducing agent to be predicted; namely, it is shown that a solution of sulfurous acid at 25° (when the corresponding pressure of sulfur dioxide is 1 atm. and the H^+ concentration is 1 molal) may oxidize any other oxidation–reduction combination which has a reduction potential more reducing (less negative) than —0.37 volt, and that it may reduce any combination which has a potential more oxidizing (more negative) than —0.14 volt. Therefore it may either oxidize or reduce any combination with a potential between —0.37 and —0.14 volt; which of these two possible effects actually occurs will depend on the relative rates of the oxidizing reaction and the reducing reaction.

PASADENA. CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAPE TOWN]

THE SINGLE POTENTIAL OF THE NICKEL ELECTRODE

BY EDGAR NEWBERY

RECEIVED JANUARY 10, 1929 PUBLISHED MAY 6, 1929

The single potential of nickel has been the subject of numerous investigations during the past thirty-five years but so far no work has been done which has inspired sufficient confidence for the values obtained to be accepted as standard. Each investigator claims accurate reproducibility for his particular results and yet the variety of opinion is surprising. Some give positive values, some negative, and the range between extremes is of the order of one volt. The whole position is therefore highly unsatisfactory and the following work was undertaken with the view in the first place of investigating the reasons for these extraordinary variations and in the second place of deciding whether it is possible to assign any definite single potential to this metal.

Possible sources of variations in results are: (1) impurities in the electrode, (2) impurities in the electrolyte, (3) variations in nature of electrode surface, (4) changes in electrolyte during measurements, and (5) chemical action between electrode and electrolyte.

1. Pure nickel free from cobalt and iron has been used by most of the investigators. In the course of this work various samples from the purest available to markedly impure material containing iron, cobalt and up to 2% of copper were used, but no difference could be detected which could be ascribed definitely to these impurities. Extreme purity of nickel from other metals appears therefore to be of small importance for the purpose in hand.

Gaseous impurities, however, are in another category. Experiments were tried using the carefully cleaned metal in an atmosphere of nitrogen with air-free solutions. When air was admitted and even bubbled through the solution, no change could be detected. Oxygen is therefore an unimportant impurity, contrary to the opinion of certain investigators. On the other hand, hydrogen has a powerful effect. This gas is very appreciably soluble in metallic nickel and if present in any considerable quantity may transform the nickel into a hydrogen electrode. Freshly prepared electrolytic nickel contains large quantities of hydrogen and the single potential of such an electrode may differ by as much as 0.5 volt from that of a similar electrode free from the gas. Hydrogen is therefore a dangerous impurity and must be rigidly excluded. The values recently obtained by K. Murata[1] are invalidated for this reason.

2. Chemically pure nickel salts are available but preliminary experiments tried with crude commercial samples showed no variations which

---

[1] **Murata,** *Bull. Chem. Soc. Japan,* **3,** 57–69 **(1928).**

could be definitely ascribed to this source. Extreme purity of the electrolyte appears therefore to be a matter of little importance.

3. In the case of copper, recently investigated, it was found that variations in the nature of the electrode surface had little or no effect upon the single potential. In striking contrast to this, it has been found that the difference of potential between a highly polished and a very rough nickel surface is of the order of 0.4 volt and further that reproducible results at any stage between these limits could be obtained by choosing different grades of emery or glass paper for preparing the surface.

4. Nickel sulfate, the salt generally used for this purpose, is very stable in solution and there appears to be no reason for ascribing any appreciable influence to this factor.

5. Judging by the rapid changes of potential which occur when a nickel electrode is first placed in a solution of a nickel salt, there is no doubt that chemical action does occur between electrode and electrolyte. Such action is, however, extremely small though its effect upon the single potential is great. A highly-polished nickel rod immersed in a solution of nickel sulfate for several hours is unchanged in appearance even under the microscope, although its single potential may have changed by 0.3 volt during the period.

Experimental

The apparatus used was identical with that previously described for copper electrodes.

Especially pure nickel sulfate free from cobalt and iron was used for making up the solutions and the electrodes were made from Merck's A.R. nickel in the form of sheet 0.5 mm. thick or small rods 2 mm. thick. The electrodes were in most cases covered with hard white sealing wax leaving 1 sq. cm. exposed. This was done in order to avoid the possible interference of surface actions at the liquid–air boundary, but it is probable that this precaution is unnecessary.

It is essential that electrodes be kept in motion with respect to electrolyte during observations of single potential. An electrode which has been left at rest for some time in the electrolyte shows a sudden change of potential of the order of 0.2 volt when moved. This is most probably due to local concentration changes in the film of electrolyte in contact with the electrode and such changes can only be avoided by rapid relative motion between electrode and electrolyte. Where rods were used, they were rotated at speeds of about 500 r. p. m., and where plates were used a small spiral glass stirrer was rotated at the same speed close in front of the plate.

(a) In view of the success of Nielsen and Brown[2] in preparing a standard copper electrode by using a two-phase amalgam, this method was adopted for the first mode of attack. The amalgam was prepared by electrolyzing a solution of pure nickel chloride using a cathode of especially pure electrolytic mercury and an anode of pure sheet nickel. After washing, the amalgam was heated to the boiling point of mercury to expel any traces of hydrogen, and preserved under a half-molar solution of nickel sulfate.

The cell $\mathrm{NiHg} \mid \mathrm{NiSO_4}\ M/2 \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$ was then made up and immersed in a thermostat at 25°. This cell gave very erratic readings varying between 0.22 and 0.35

---

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

volt when first made up and rising to nearly 0.7 volt after standing for two hours. A small spiral glass stirrer was then introduced to stir the amalgam surface during observations. The readings then obtained were much steadier but still varied between 0.4 and 0.55 volt. Similar experiments with more dilute amalgam gave similar results. With the use of twentieth molar nickel sulfate solution, still more erratic values were obtained.

A dropping electrode was then tried for the amalgam but the values given were extremely irregular, varying between 0.3 and 0.65 volt for no apparent reason. Further work with the amalgam was therefore abandoned.

(b) The method which proved successful with copper whereby the "instantaneous" potential of a rapidly rotating rod is measured during the actual process of immersion was now tried.

The cell used was Ni | $NiSO_4$ $M/2$ | Hg_2SO_4 | Hg, the mercury electrode being contained in a separate vessel communicating with the main vessel through 25 cm. of 1-mm. tubing, and the whole apparatus immersed in a thermostat at 25°.

The rotating electrode holder was attached to a stand fitted with rack and pinion for raising and lowering, and the main vessel was closed with a cork through which a glass tube passed, just wide enough to admit the rotating electrode. Other tubes allowed the vessel to be filled with air or nitrogen at will.

It was soon found that reproducible results could be obtained if the electrode was prepared in the same way, even with different samples of metal, some of which were certainly impure. If, however, the method of preparation of the surface was varied, the values obtained also varied widely. For each abrading or polishing material used, there appears to be a fairly definite limiting potential produced. With the finer polishing agents this limit is only obtained after long-continued and repeated application, whereas the coarser agents give a constant value at once. The values obtained with the various agents are given in the following table.

Polishing agent	E.m.f. of cell, volt	Polishing agent	E.m.f. of cell, volt
No. 1 emery cloth	0.63	Soft filter paper	0.45
No. 00 emery cloth	.59	Agate burnishers	.40
No. 000 emery paper	.56	Agate followed by selvyt cloth	.25

Since it was found that the value of 0.45 volt could be repeatedly obtained by using a certain sample of filter paper, various modifications were introduced while keeping to this polishing agent. (1) Previous heating of the electrode to redness in high vacuum had no effect. (2) Previous boiling of the solutions, cooling in an atmosphere of nitrogen and carrying out the measurements in an atmosphere of nitrogen had no effect. **(3)** Immersing the electrode in concentrated potassium hydroxide solution, washing and drying, lowered the e.m.f. of the cell from 0.45 to 0.40 volt. (4) On allowing the rotating electrode to remain in the solution, a fairly rapid rise to 0.53 volt occurs. (5) After (3) above, the electrode was abraded with No. 1 emery cloth, when the value 0.63 volt was again obtained. (6) Repeating (4) with the electrode after (5) treatment, a *fall* to 0.53 volt was observed.

From the above observations we conclude (1) that the presence of oxygen has no appreciable effect upon the single potential of nickel, (2) that immersion in alkali does not render nickel passive, since the single potential of passive nickel differs from that observed by about 1.2 volts and **(3)** that the value of 0.53 volt appears to be some kind of equilibrium value for the cell.

(c) The experimental electrode was now fitted up in a cell containing 0.5 M nickel sulfate together with a secondary nickel electrode and a standard mercurous sulfate electrode and connected to a commutator circuit for measuring back e.m.f., just as has been employed for measuring over-voltage.

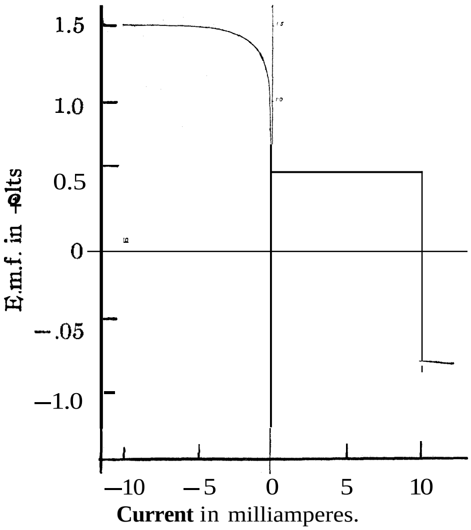


Fig. 1.

When the experimental electrode was made the cathode, the back e.m.f. of the cell rose very rapidly to over 1 volt with a current of 0.1 milliampere and hydrogen gas was liberated. When the same electrode was made the anode, the back e.m.f. fell slowly to 0.53 volt with a current of *2* milliamperes, then rose to 0.55 volt with a current of 4 milliamperes and retained this value up to a current of 10 milliamperes. At this stage after passing current for about one minute the back e.m.f. suddenly changed from 0.55 volt to -0.81 volt due to the electrode becoming passive. The accompanying curve illustrates these changes and should be compared with that obtained for copper in the same way.

These experiments show very clearly the dangerous nature of hydrogen as an impurity when measuring the single potential of nickel. A current of 10^{-5} ampere is sufficient to alter the value by 0.1 volt when the nickel is the cathode, whereas the value is nearly constant when the nickel is the anode until the current passing is one thousand times as great as this. It should be emphasized that no current is passing during the actual measurement of the above potentials. The constancy of the values under anodic treatment appears to be due to the slow continuous removal of the surface of the nickel leaving a clean surface always exposed to the electrolyte. Only under these conditions are the rapid fluctuations of single potential suppressed and constant reproducible values obtained.

Deductions from the Experimental Results.—The cell Ni | $NiSO_4$ $M/2$ | Hg_2SO_4 | Hg shows three distinct values under different conditions, two limiting values of approximately 0.26 and 0.65 volt and one somewhat persistent intermediate value of 0.53 volt at 25°.

Assuming the nickel salt to be 25% dissociated, the single potential of the mercury electrode is 0.96 volt referred to the normal calomel electrode as 0.56 volt. Hence the single potential of nickel in contact with a normal solution of nickel ions will be 0.73, 0.33 or 0.45 volt referred to normal calomel electrode=0.56 volt, and 0.45, 0.05 or 0.17 volt referred to normal hydrogen electrode=0.00 volt. In order to explain the existence of three values for one metal it is necessary first to note that the variability of the results obtained when nickel amalgam is used in a dropping electrode indicates that the variations are inherent in the nickel itself and are not due solely to interaction between electrode and electrolyte. Again, the extreme values are obtained at will by extreme polish or extreme roughness. It is well known that in polishing a metal the crystals are pressed down and the amorphous binding material is smoothed over the top of them. The obvious conclusion to draw, therefore, is that amorphous and crystalline nickel have different solution pressures and therefore different normal single potentials. These are 0.73 and 0.33 volt, respectively, whereas the intermediate value of 0.45 volt represents that of the equilibrium mixture normally present throughout the mass of the nickel. An objection to this theory may be made that in the amalgam it is not possible to have amorphous and crystalline nickel present at the same time. If, however, we call the two allotropes a-nickel and β-nickel, respectively, it is not necessary to postulate that these are identical with the amorphous and crystalline phases, but merely that the concentration of the a-nickel is higher in the amorphous phase and that of β-nickel in the crystalline. Both types may therefore retain their identity even when dissolved in mercury.

The extreme values found for the single potential will therefore still represent those of mixtures and not of pure a- and β-nickel. Since the experimental values are 0.45 and 0.05 volt, respectively, referred to the hydrogen electrode, we may safely put down the single potential of α-nickel as at least 0.5 volt and that of 0-nickel as approximately equal to that of hydrogen.

In the solution the existence of a-nickel is doubtful. If present at all it must be in very small proportions since no appreciable quantities of nickel are deposited in a nickel-plating cell until the applied e.m.f. greatly exceeds that theoretically needed for a metal with a single potential of 0.5 volt. β-Nickel and hydrogen are then deposited together; the hydrogen escapes and the β-nickel reverts to the equilibrium mixture of a- and β- by a comparatively slow change. These processes greatly hinder the formation of large crystals and thus produce a marked tendency to the production of smooth polished deposits. In addition, the escape of hydrogen, together with the rearrangement of the deposited metal, results in a contraction of the metal with consequent tendency to strip off the base metal, especially if the deposit is thick.

The suggestion that nickel contains two allotropic forms is not new. Others have used it in attempts to explain the passivity and the overvoltage of nickel and Glasstone[3] has used it to explain the retardation phenomena shown during electrolytic deposition of the iron group metals. If a current of about 0.02 amp. be passed between two nickel electrodes each of 1 sq. cm. surface in a neutral solution of nickel sulfate, hydrogen is liberated at one electrode, which then exhibits overvoltage, and oxygen at the other, which becomes passive. The back e.m.f. of this cell then exceeds 2.2 volts, the single potential of the cathode being at least 0.7 volt below that ascribed to β-nickel and that of the anode 1.0 volt above that ascribed to a-nickel. As an explanation of overvoltage or passivity, therefore, such a theory is untenable. As an explanation of the retardation phenomena along the lines suggested by Glasstone it is equally untenable. If β-nickel in solution requires the application of an e.m.f. similar to that needed for zinc to deposit it on a cathode, then in a solution containing zinc and nickel in equal proportions, a high current density should deposit the two metals in approximately equal quantity and the relative proportions should not vary greatly with change of current density. Such is far from being the case. It is found in practice that at the cathode of such a cell the proportion of nickel and of hydrogen relative to zinc becomes rapidly less as the current density increases and at a very high current density (200 to 600 amps. per sq. ft.) nearly pure zinc is deposited with high current efficiency. This shows that both nickel and hydrogen are subject to some powerful retarding force which increases with current density and which does not affect zinc. The hydrogen ion is almost certainly hydrated. When deposited on the cathode it must lose its water of hydration before it can form gaseous hydrogen—a process requiring time. If a part of the current is being carried by a non-hydrated ion at the same time, it is evident that at higher current densities a greater proportion of the current will be carried by the non-hydrated ion. Zinc appears to be such a non-hydrated ion, whereas nickel appears to be hydrated in a similar way to hydrogen.[4] The retardation phenomena observed with hydrogen and all the iron group metals are therefore to be explained on the basis of hydration of the ions. At higher temperatures the velocity of dehydration of the ions will increase and therefore the retarding forces will decrease, as has been observed by Glasstone.[3]

---

[3] Glasstone, J. Chem. *Soc.*, 129,2896 (1926).

[4] The term "hydration" here implies true chemical hydration and not mere surface adsorption. The hydration of the ions of the alkali metals, halogens, etc., which is assumed in order to explain anomalies in ionic velocities must be of an entirely different nature.

The variations of single potential of a nickel electrode in a solution of *a* nickel salt appear to be due to a variety of causes. If the surface is highly polished, the surface film contains excess of α-nickel and the potential first observed will be too high. This film is extremely thin and very slight attack by the electrolyte will be sufficient to expose the underlying @-nickel, with consequent fall of single potential. If the electrode is at rest, an interchange of ions with the solution occurs, but the ions received will be hydrated while those expelled will be non-hydrated. There will therefore be an accumulation of non-hydrated ions in the solution and an accumulation of water in contact with the electrode. At the same time a film of basic salt may form around the electrode and thus change the ionic concentration of the solution. Hence motion of the electrode with respect to the electrolyte may produce large changes of single potential, and the equilibrium potential of a stationary electrode will be very different from that of a rotating electrode.

Iwaśe and Miyazaki[5] have recently found that the single potential of an iron single crystal is much greater and more constant than that of polycrystalline iron. Hence the above theory will also apply to iron and probably to cobalt.

It appears probable that the true reversible single potential of a metal cannot be determined directly if that metal gives rise to hydrated ions.

Summary

The single potential of nickel in a solution of nickel sulfate has been measured by three distinct methods under very varied conditions. The values obtained vary greatly with the condition of the electrode surface, with time and with relative motion between electrode and electrolyte.

Constant and reproducible values are obtained when the nickel is treated anodically with a small current density insufficient to produce passivity, the potential being measured when the current is not passing. Whether these values represent true reversible potentials or not is open to question. Nickel amalgam is even more erratic than massive nickel when used for single potential measurements.

It is suggested that solid nickel contains two allotropes having normal single potentials of approximately + 0.5 and 0.0 volt, respectively, referred to the normal hydrogen electrode. The equilibrium mixture of the two allotropes normally present in massive nickel has a corresponding potential of 0.17 volt.

On the basis of the above theory, together with that of the hydration of nickel ions, an explanation is offered (1) of the observed variations of single potential, (2) of the retardation phenomena observed during elec-

---

[5] Iwaśe and Miyazaki, *Science Repts. Tôhoku Imp. Univ.*, *17*, 163 (1928).

trolytic deposition of nickel and *(3)* of the electrodeposition of nickel in a polished condition.

CAPE TOWN, SOUTH AFRICA

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

AN ISOTOPE OF OXYGEN, MASS 18. INTERPRETATION OF THE ATMOSPHERIC ABSORPTION BANDS

BY W. F. GIAUQUE AND H. L. JOHNSTON

RECEIVED JANUARY 14, 1929 PUBLISHED MAY 6, 1929

In connection with our study of the entropies of gases we have recently considered the available spectroscopic data for oxygen. The atmospheric absorption bands of oxygen contain the necessary information concerning the rotation levels of the oxygen molecule but we found that no completely satisfactory interpretation of these bands has been given, although Mulliken[1] has recently arrived at a partial solution. However, he expresses the opinion that a revised interpretation will probably be necessary in order to include a weak band for which no explanation has been offered by any previous worker.

We can have little confidence in an entropy calculation based on uncertain interpretation since a misunderstood multiplicity would introduce a serious error in our result. We were thus led to a further study of the data.

We may say at once that, in view of our result, no revision of Mulliken's interpretation is necessary.

The most accurate data are those of Dieke and Babcock[2] so they alone have been considered.

The absorption bands are due to a 1.6-volt excitation from the various rotation levels of the normal oxygen molecule, to the various rotation levels of several vibration states of the 1.6-volt level. Only the alternate rotation levels are present, as would be expected for a non-polar molecule with two non-spinning nuclei. All of the lines of the bands, which are of the P and R types, appear as doublets and in addition a weak band is present, the "A' band," which appears to be an exact duplication of the A band except that the rotation lines have a different spacing.

Our principal problem was to decide whether the A and the A' bands originated from a common source or not. We tried many ways of combining the lines both within the strong A and the weak A' bands, respectively, and also combining weak with strong but could find no scheme that would account for the bands arising from a single molecular form. Mulliken considers that the normal oxygen molecule must be a triplet

[1] **Mulliken,** *Phys.* ***Rev.,*** **32,** *880* **(1928).**

[2] **Dieke and Babcock,** *Proc. Nat. Acad. Sci., 13, 670 (1927).*

S state and mentions the previous workers who have concluded this from the various spectroscopic observations and magnetic susceptibility data. The upper state of the atmospheric bands is a singlet S state. A triplet S state results from two unbalanced spinning electrons coupled together and having three possible orientations. One of these, called the F_1 state, has the spin momentum with the molecular rotation; in the F_3 state the spin is against the molecular rotation and the F_2 state has the spin approximately at right angles to the axis of the molecular rotation. With the above scheme Mulliken fully explains all of the observed lines of the A band and also the absence of the first line of the P_2 series. It is noteworthy that the energies accompanying the extremely loose couplings of the spin with the weak magnetic field, caused by the thermal rotation of the molecule, are of a reasonable amount, decreasing for F_1 states and increasing for F_3 states as the molecular rotation increases, as would be expected. This behavior is completely duplicated by the A' band except for the previously mentioned different spacing of the lines.

It occurred to us that the A' band might result from an isotope of oxygen and we have found that it is fully explained as originating from an oxygen molecule consisting of an atom of mass *16* combined with an atom of mass 18. Such an isotope has not previously been observed but its existence in small amount has certainly not been disproved. Since it is of practically the same mass as water, it might easily be misinterpreted in a mass spectrograph.

The necessary equations for this calculation have been given by Loomis.[3] The electron excitation is assumed to be identical, within the limit of error, for both the heavier and lighter molecules. Only the $^1/_2 \longrightarrow {}^1/_2$ vibration change was observed in the weak system. The vibrational isotope effect is given by the formula

$$\nu_2^{n={}^1/_2} - \nu_1^{n={}^1/_2} = (\rho - 1)\nu_1^{n={}^1/_2}$$

where $\rho = \sqrt{(M_1 + M_2)/2M_2}$ and M_1 and M_2 are the masses of the respective atoms. The rotational isotope effect is given by

$$\nu_2^m - \nu_1^m = (\rho^2 - 1)\nu_1^m$$

where m is the rotational quantum number. The symbol ν refers to the energy change divided by h for the various states concerned. The total isotope effect is the sum of the two.

Using the above formulas we obtain the following expressions for the isotopic doublets.

$$\Delta\nu_P = 2.12 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m - 1)^2 + \beta'(m - 1)^4]$$
$$\Delta\nu_R = 2.12 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m + 1)^2 + \beta'(m + 1)^4]$$
$$m = \frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \ldots$$

---

[3] Loomis, *Bull. Nat. Res. Council,* 11, Chap. V (1926).

The constants as given by Dieke and Babcock are $B'' = 1.438$, $\beta'' = 6.31 \times 10^{-6}$, $B' = 1.390$ and $\beta' = 5.75 \times 10^{-6}$.

The rotation quantum number m is retained for convenience in using the equation of Dieke and Babcock instead of using the formulation in terms of j_k as indicated by wave mechanics. $m = j_k + {}^1/_2$, where j_k is the number of units of angular momentum due to the rotation of the molecule.

The first term, 2.12 cm.$^{-1}$, in the doublet formulas is the vibrational isotope effect for the zero point state of one-half unit of vibration. Its calculation makes use of the formula given by Birge[4] for the vibration of the normal oxygen molecule

$$\nu^n = 1565.37n - 11.37n^2$$

and of that given by Dieke and Babcock[2] for the 1.6-volt level

$$\nu^n = 1415.017n - 11.91n^2 - 0.3525n^3$$

where $n = 0, 1, 2, \ldots\ldots$

In accordance with wave mechanics both of these formulas should be transposed so that the state given as zero by the formulas corresponds to $n = {}^1/_2$.

Dieke and Babcock's j numbering of the lines is correct if it is taken **as** $j(= j_k)$ of the molecule in the upper state.

The calculated and observed values are given in Table I.

TABLE I

ROTATIONAL–VIBRATIONAL ISOTOPE DOUBLETS FOR OXYGEN

j_k, normal state	Calcd. separation in cm.$^{-1}$	$P_1' - P_1$	$P_2' - P_2$	j_k, normal state	Calcd. separation in cm.$^{-1}$	$R_1' - R_1$	$R_2' - R_2$
1	2.28	2.25	Excl. transition	1	1.82	..	..
				3	1.53	..	1.49
3	2.62	2.57	2.52	5	1.27	1.28	1.27
5	2.97	2.91	2.93	7	1.03	0.95	0.93
7	3.35	3.29	3.32	9	0.81	.75	.74
9	3.75	3.70	3.72	11	.61	.59	.55
11	4.17	4.10	4.13				
13	4.61	4.55	4.57				
15	5.07	5.01	5.01				
17	5.56	5.50	5.46				

The average deviation of observed minus calculated separations is -0.05 cm.$^{-1}$. The maximum deviation is -0.13 cm.$^{-1}$. This is well within the limit of accuracy of the data and is certainly better than we had expected in view of Dieke and Babcock's remarks about the accuracy.

We would obtain about the same p from a 17–17 molecule but calculation shows a poorer agreement with the data and the chance of formation of such molecules rather than 16–17 molecules seems definitely to eliminate it as a possibility. No other possibility would give even rough agree-

Birge, *Bull. Nat.* Res. *Council, 11,* Chap. *V (1926).*

ment. We are thus forced to conclude that an isotope of oxygen, mass 18, exists in the earth's atmosphere. From the relative intensities of the bands the amount must be very small and would thus be difficult to detect in a mass spectrograph. It seems possible that the 16–18 molecule might be a more efficient absorber of radiation than the 16–16 molecule due to the slight polarity introduced by the zero point vibration; thus relative intensities may be taken as an upper limit to the amount of 16–18 oxygen present.

Our conclusions are supported by the absence of the excluded line in the A' band which would correspond to the $j'' = 0 \rightarrow j' = 0$ transition, as was pointed out by Mulliken. It may also be noted that the vibrational and rotational isotope effects considered independently are in agreement. For example, $I_{18-16}/I_{16-16} = 1.059$ is the theoretical ratio of the two moments of inertia, while Dieke and Babcock's constants give 1.062 for the ratio in the normal state and 1.060 for the 1.6-volt level.

Addendum

Since the above paper was written, we have communicated with Mr. H. D. Babcock, of Mount Wilson Observatory, who has kindly placed some additional material in our hands. This consists of thirty-four weak lines and we have found that twenty-seven of these are due to the 16–18 oxygen molecule, being the alternate lines in the P_1', P_2', R_1' and R_2' series referred to above. This is in accordance with the predictions of wave mechanics since when the two ends of a molecule are different, all the rotation levels should be present. Since the lines corresponding to these new members of the above series do not occur in the 16–16 band, isotopic doublets are not observed in this case We have, therefore, made use of the equations given by Dieke and Babcock for the 16-16 molecule combined with the isotope effect to calculate the wave numbers to be expected for the new lines. In making this calculation we found that the equations of Dieke and Babcock did not reproduce their published data with sufficient accuracy for our purpose so we made use of a linear deviation plot in calculating the positions of the new lines.

The observed and calculated values are given below in Table II. The designations are in accordance with those used by Dieke and Babcock.[2]

The quantum number j refers to the rotation state in the upper electronic level. The symbol b indicates that an observed line has been used in two places and bb indicates use in three places. The symbol d is used where the line is known to be double. A number of the missing lines have undoubtedly been obscured by near coincidence with strong lines of the A band.

The seven unexplained lines which do not necessarily belong to oxygen are given in Table III.

TABLE II

OBSERVED LINES DUE TO 16–18 OXYGEN MOLECULE COMPARED WITH VALUES CALCULATED FROM 16–16 MOLECULE DATA

P_1' (j)	λ	$\nu_{\text{vac.}}$	$\nu_{\text{calcd.}}$
1	7,621.312	13,117.50	13,117.49
3	......	......	111.64
5	.....	......	105.44
7	32.150	13,098.87*b*	13,098.89
9	.....	......	91.99
11	40.47	84.60	84.72
13	44 90	77 02	77.11
15	49.581	69 02	69 14
P_2' (j)			
1	7,620.064	13,119.64	13,119.58
3	23.540	113.56	113.72
5	.....	......	107.48
7	31.021	100.81*b*	100.90
9	.....	......	13,093.96
11	39.32	13,086.57	86.66
13	43.79	78.92	79.01
15	48.46	70.94	71.01
17	53.34	62.60	62.66
R_1' (j)			
1	.....	......	13,125.74
3	7,613.569	13,130.83	130.64
5	11.002	135.26	135.30
7	08.552*d*	139.49*b*	139.61
9	06.211*d*	143.54*b*	143.54
11	04 2	147.0	147.14
13	02.346	150.22*b*	150.33
15	.....	......	153.19
17	7,599.215	155.64	155.66
19	.....	......	157.77
21	96.965	159.54	159.51
23	96.208d	160.85*bb*	160.92
25	95.579	161.94	161 94
27	95.245	162.51*bb*	162 60
R_2' (j)			
1	7,615.553	13,127.42[a]	13,127.65
3	12.574	132.55	132.59
5	09.840	137.26	137.27
7	07.358	141.55*b*	141.60
9	05.068	145.50	145.55
11	02.996	149.10	149.18
13	01.118	152.34	152.39
15	7,599.449	155.23	155.27
17	97.995	157.75	157.75
19	96.750	159.91	159.89
21	95.759	161.62*b*	161.66
23	94.970	162.99*bb*	163.08
25	94.284	164.18	164.14
27	93.848	164.94	164.82

[a] Possibly beginning state anomaly.

TABLE III

UNEXPLAINED LINES

λ	7,641.53*d*[a]	40.25	37.172*d*[a]	35.9	20.507	13.246	60.5
$\nu_{\text{vac.}}$	13,082.79	84.98	90.25	92.44	118.88	131.39	143.0

[a] Close double used once in description of A' band.

Babcock has also estimated the relative intensities of A' and A lines as roughly 1% and that the odd and even members of the A' band are of about equal intensity. As we have pointed out in the above paper this probably cannot be taken as a measure of the relative amounts since the absorption coefficients may be quite different. Assuming that the two sorts of molecules did exist in the above proportions, the lighter isotope of oxygen would have an atomic weight of about 15.98. This is obtained due to the existence of twice as many levels in the 16–18 molecule, thus making the total absorption 2% of that due to 16–16 oxygen. The mass spectrograph results obtained by Aston in terms of the lighter isotope seem to fall too close to the atomic weight values based on other methods to permit a value of 15.98 for the light isotope of oxygen. The situation is complicated by the possibility of isotopes of all the light elements but the general agreement seems significant. Aston has pointed out that it is very difficult to prove the non-existence of other isotopes of oxygen with the mass spectrograph. However, this appears to be the most promising possibility for the estimation of the relative amount of O^{18}.

The presence of isotopes of oxygen will, of course, not affect chemical atomic weights except in the remote possibility of non-uniform distribution but before we can know the relationship between ordinary atomic weights and the results of the mass spectrograph, the amount of O^{18} must be known.

Another point of interest in connection with the new lines is as follows. If P, Q and R branches resulted from each of the triplet states of the oxygen molecule, we would have nine branches. Only four branches have been observed. This seems to indicate that the rotational momentum is required to change by an amount of plus or minus one that is, $\Delta j_k = *1$ in addition to the usual requirement $\Delta j = \pm 1$ or 0. Professor R. S. Mulliken of the University of Chicago has called our attention to the similarity of the above selection rule to that in the atomic case where for line spectra $\Delta l = \pm 1$ and $\Delta j = \pm 1$ or 0.

Summary

The weak band in the atmospheric absorption of oxygen has been explained and demonstrates the existence of an isotope of oxygen, mass 18, present in small amount.

BERKELEY, CALIFORNIA

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

THE HEAT CAPACITY OF HYDROGEN IODIDE FROM 15°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

BY W. F. GIAUQUE AND R. WIEBE

RECEIVED JANUARY 14, 1929 PUBLISHED MAY 6, 1929

We have previously shown[1] that for hydrogen chloride and for hydrogen bromide the entropies as calculated for the gaseous state with the assistance of spectroscopic data are in agreement with those obtained from our calorimetric measurements and the third law of thermodynamics. This paper contains similar calorimetric data for hydrogen iodide, again leading to agreement between the two methods of obtaining the entropy.

Preparation of Hydrogen Iodide.—Hydrogen iodide was prepared directly from the elements in a manner very similar to that used for the preparation of hydrogen bromide. Iodine was sublimed into a large tube which was attached to a reaction tube containing a platinum spiral wound on quartz. The whole apparatus was then immersed in a water-bath which was kept at the boiling point by electrical heating of the platinum

---

[1] Giauque and Wiebe, THIS JOURNAL, (a) 50, 101 (1928); (b) 50, 2193 (1928).

spiral to about 600°. Hydrogen was prepared by electrolysis and freed of oxygen by means of a nickel catalyst. Dry hydrogen was passed into the tube containing the iodine and became saturated at 100°. This left a large excess of hydrogen, which we considered desirable. The mixture passed over the hot platinum spiral and then through a trap surrounded by salt and ice to condense the considerable amount of unreacted iodine which was to be expected from the known equilibrium. The hydrogen iodide containing some iodine was finally condensed in a trap surrounded by liquid air, the hydrogen being allowed to escape. After a rough distillation had removed most of the iodine, the material was distilled into a bulb containing mercury which had been distilled onto the walls. This was very effectivein eliminating all trace of color, leaving an exceptionally clear liquid. The hydrogen iodide, which could at most have contained only a trace of water, was then distilled into a bulb containing a sufficiently large amount of phosphorus pentoxide to bring it into intimate contact with all of the liquid. The drying continued for about a week. It was kept cold with the assistance of a carbon dioxide and ether bath. This solidified the hydrogen iodide which was, however, frequently melted and kept melted over considerable periods. The material was then distilled several times, the end fractions being discarded. All of the above operations were carried out in a vacuum-tight system which was evacuated by means of a mercury diffusion pump.

TABLE I

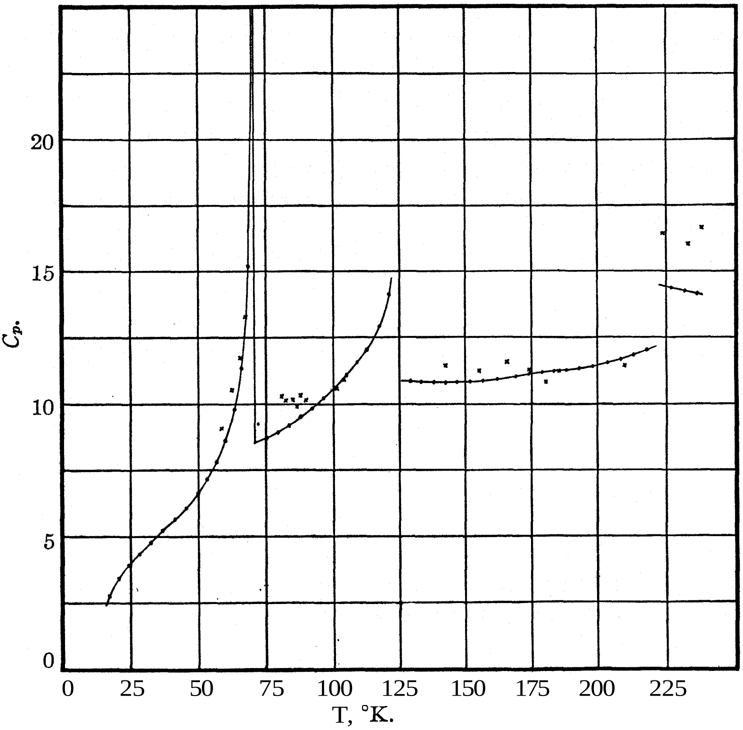
HEAT CAPACITY OF HYDROGEN IODIDE

Molecular weight, 127.94

T. °K.	AT	C_p/mole in cal./deg.	T, °K.	AT	C_p/mole in cal./deg.
17.11	3.611	2.745	117.32	3.979	12.96
20.37	2.734	3.426	121.15	3.639	14.11
24.03	3.957	3.947	129.21	4.342	10.87
28.05	3.956	4.384	133.54	4.100	10.85
32.29	4.256	4.834	138.13	4.785	10.83
36.73	4.392	5.255	142.61	3.924	10.81
41.25	4.535	5.696	147.01	4.570	10.83
45.58	3.982	6.092	151.72	4.483	10.84
49.76	4.219	6.625	156.74	5.144	10.85
53.01	3.823	7.165	162.10	4.986	10 94
56.79	3.416	7.812	169.07	5.199	11.07
60.11	3.074	8.631	174.23	4 694	11.13
63.22	3.050	9.802	179.10	4.579	11.20
66.09	2.643	11.37	183.96	4.485	11.22
68.47	2.082	15.23	188.71	4.362	11.26
70.12	1.067	32.52	193.51	4 242	11.33
72.09	2.880	9.274	198.46	4.865	11.38
75.33	3.961	8.727	203.57	4.728	11.56
79.56	4.334	8.928	208.53	4.587	11.63
83.83	4.063	9.221	213.30	4.450	11.81
87.93	3.812	9.563	218.00	4.303	12.04
92.18	4.548	9.807	222.31	Melting point	
96.37	3.620	10.24	227.05	4.263	14.34
100.69	4.454	10.56	231.67	4.241	14 26
105.02	4.023	11.08	236.15	4 190	14 15
108.97	3.764	11.57	237.75	Boiling point	
113.12	4.300	12.04			

Heat Capacity Measurements.—The calorimetric measurements were all made with gold calorimeter II. The calorimeter and experimental method have been described in our previous paper.[1a] 1.9662 moles of hydrogen iodide were used for the measurements. The data are given in Table I.

The data are shown graphically in Fig. 1, which also includes the data of Eucken and Karwat,[2] who investigated this substance from 58°K. to its boiling point. Most of our data are accurate to two- or three-tenths of one per cent. Some points near 175°K. are probably off by about five-tenths of one per cent. due to small distillation heat effects. The measurement at 17.11°K. may be in error by one per cent.



×, Eucken and Karwat; ●, Giauque and Wiebe.

Fig. 1.—Heat capacity in calories per mole of hydrogen iodide.

The Transitions of Hydrogen Iodide.—Hydrogen iodide has two gradual transitions similar to those found for hydrogen bromide. In our previous discussion of the transitions of hydrogen bromide, we mentioned that lack of equilibrium was a factor, although we believed that the transitions would be gradual even with complete equilibrium. We have

---

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

learned nothing from hydrogen iodide to change this opinion but some measurements on the transition occurring near 125°K. supply interesting information concerning the difficulty in obtaining true equilibrium and also show that a considerable amount of energy is absorbed within a very small temperature range if not at a definite temperature. Starting at a temperature of 122.99°K., 55.8 cal. per mole of substance was added over a period of ten minutes. At two minutes after energy input ceased, the temperature was 125.73°K., and this decreased at a gradually diminishing rate to 125.64°K. in seventy minutes, at which time the rate of decrease was 0.0004" per minute. The current was again passed through the heater adding 56.6 cal. per mole over a period of ten minutes. At two minutes after energy input ceased, the temperature was 125.88°K. and decreased to 125.64°K. in twenty minutes, at which time the rate of decrease was 0.004" per minute or ten times the previous rate at this temperature. At fifty minutes it had decreased to 125.60" and the rate of decrease was 0.0008" per minute. It is evident that as the transition approaches completion, equilibrium is obtained more readily. The results suggest the following possibility: the transition starts as a changing thermal equilibrium between energy states of the hydrogen iodide molecule, both in the same crystal lattice, but when a sufficient concentration of the higher energy state has been reached, the system becomes unstable and changes to a new crystalline form. This question could be investigated by X-ray measurements of crystal structure, although care might be necessary in cooling the hydrogen iodide slowly through the transition range if our conditions were to be duplicated. Simon and Simson[3] have found by X-ray analysis that the somewhat similar transition of ammonium chloride is not accompanied by a change in crystalline form and they conclude that it represents an equilibrium between molecular energy states.

It seems probable that many substances will have a change of phase induced by an increasing concentration of molecules with some degree of freedom excited in addition to the ordinary vibration.

The heat capacity measurements in the transition ranges were not used in obtaining the entropy, for which purpose separate determinations of total heat input over the whole range were obtained. The values are given in Table II.

TABLE II

HEAT ABSORBED IN TRANSITION REGIONS OF HYDROGEN IODIDE

Temp. interval, °K.	60.90–72.23	62.09–75.42	113.75–129.63	113.26–129.11
Heat absorbed, cal./mole	150.8	167.4	394.6	393.8

Heat of Fusion.—Two determinations of the heat of fusion gave 687.1 and 685.5 cal. per mole, respectively. The average is 686.3 ± 0.8

---

[3] **Simon and** Simson, *Naturwissenschaften,* **38, 880** (1926).

cal. per mole. Comparison with the results of previous observers is made in Table III.

TABLE III

HEAT OF FUSION OF HYDROGEN IODIDE

Melting point, 222.31°K. Molecular weight, 127.94

Heat of fusion, cal./mole	Observer
552	Beckman and Waentig[4] (1910)
732, 688 (weighted mean, 726)	Eucken and Karwat[2] (1924)
687.1, 685.5 (mean, 686.3 ± 0.8)	Giauque and Wiebe (1929)

Melting- and Boiling-Point Temperatures of Hydrogen Iodide.—The melting point was observed with one-fourth, one-half and two-thirds of the material melted, respectively. The observations covered a period of six hours. The maximum deviation was 0.006" on the thermocouple and 0.004" on the resistance thermometer. The average deviation was 0.003" on the thermocouple and 0.002" on the resistance thermometer. The melting-point temperature was found to be 222.31 ± 0.05°K.

The boiling point was found to be 237.75 ± 0.05°K. This was obtained from measurements of pressure and temperature made in connection with the heat of vaporization determinations. The values obtained for the melting- and boiling-point temperatures by various observers are summarized in Table IV.

TABLE IV

MELTING- AND BOILING-POINT TEMPERATURES OF HYDROGEN IODIDE

Melting point, °K.	Melting point. °K.	Observer
222.3	238.96 (730.4 mm.)	(1897) Estreicher[5]
222.8	236.4 (751.4 mm.)	(1900) Ladenburg and Krügel[6]
222.3	237.4	(1906) McIntosh, Steel and Archibald[7]
227.1	....	(1911) Bagster[8]
222.4	237.3	(1924) Henglein[9]
223.1	237.1	(1925) Miravalles and Moles[10]
222.31 ± 0.05	237.75 ± 0.05	(1929) Giauque and Wiebe

Measurement of Amount of Hydrogen Iodide.—The amount of hydrogen iodide was measured by absorption in 30% sodium hydroxide after passing through a very small mercury trap, as was described for hydrogen chloride."' However, in this case we met a difficulty which was not encountered in the measurements on hydrogen chloride or hydrogen bromide. It was noticed that very small bubbles of gas rose slowly through the

---

[4] Beckmann and Waentig, Z. *anorg. chem.*, *67*, 17 (1910).

[5] Estreicher, *Z. physik. Chem.*, *20*, 605 (1896).

[6] Ladenburg and Krügel, *Ber.*, 33, 637 (1900).

[7] McIntosh, Steele and Archibald, *Z. physik. Chem.*, *55*, 129 (1906).

[8] Bagster, *Tab. Ann.*, 82 (1911).

[9] Henglein, *Z. Physik*, 18, 64 (1924).

[10] Miravalles and Moles, *Anales soc. españ. fís. quim.*, 23, 509 (1925).

sodium hydroxide to the surface and on testing the gas in the absorption bulb it proved to be hydrogen. The dissolved mercury was in the form of the very stable iodide complex which could not be precipitated by the addition of sulfide ion. Consequently the analysis was carried out by means of a zinc–copper couple. The effectiveness of this method was tested by duplicating the solutions except that known amounts of mercuric iodide complex were present. It was found that the method (in the rather rough manner in which we used it and for the amounts concerned) gave results 10% too low and the analyses were calculated on this basis. This was sufficiently accurate for our purpose since the total correction for hydrogen lost proved to be almost negligible. However, the evolution of hydrogen gave rise to another more serious difficulty, since during the initial weighing of the absorption bulb, the gas space was filled with air; while during the final weighing, it was nearly all hydrogen. The relative amounts of air and hydrogen in the gas space were determined and the correction was made. The total correction due to these two effects was about 0.2 of 1%.

Heat of Vaporization.—The heat of vaporization was measured by Method II, as described for the hydrogen chloride measurements.[10] The data are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN IODIDE

Boiling point, 237.75°K. Molecular weight, 127.94

HI evap., moles	0.1777	0.3014	0.3010	0.3000	
Type of run	II	II	II	II	
Time of energy input, min.	55	75	75	75	
AH at 760 mm., cal./mole	4718	4719	4732	4726	Mean, 4724 ± 5

Comparison with the results of previous observers is made in Table VI. All of the results listed are from calorimetric determinations.

TABLE VI

HEAT OF VAPORIZATION OF HYDROGEN IODIDE

Heat of vap., cal./mole	Observer
4480	(1908) Elliot and McIntosh[11]
4340	(1910) Estreicher and Schnerr[12]
4950	(1912) Beckmann[13]
5885	(1916) Cederberg[14]
4724 ± 5	(1929) Giauque and Wiebe

The Entropy of Hydrogen Iodide from the Third Law.—The entropy was obtained by graphical integration of the heat capacity against the

---

[11] Elliot and McIntosh, J. *phys. chem.*, 12, 163 (1908).

[12] Estreicher and Schnerr, *Krakauer Anz.*, 345 (1910).

[13] Beckmann, *Z. anorg. chem.*, *74*, 300 (1912).

[14] Cederberg, *Ber. chem. affin.*, Berlin, 1916.

logarithm of the absolute temperature. The method used for the two gradual transitions was the same as that previously described for hydrogen bromide. All energy above a value of 16 cal. per degree per mole was divided by the temperature selected as a center of gravity on a $(C_p - 16)$ against T plot. The temperatures selected are not to be confused with the transition temperature of ordinary "sharp transitions," nor are the heats to be taken as heats of transition, especially since the value of 16 cal. per degree subtracted over the range was purely arbitrary.

The extrapolation below 15.3°K. was carried out by means of a Debye curve with an $h\nu/k = 73$. The similarity of the heat capacity curve to those of hydrogen chloride and hydrogen bromide gives us considerable confidence in the extrapolation of the somewhat greater amount of entropy due to the lower characteristic frequency of this substance. A summary of the entropy calculation is given in Table VII.

TABLE VII

CALCULATION OF THE MOLAL ENTROPY OF HYDROGEN IODIDE GAS

0-15.3°K., extrapolation	1.085	
Transition 18.6/70.1	0.265	
Transition 192.4/125.6	1.531	
Transitions are $\int (C_p - 16)dT$, 15.3-222.31°K., graphical	20.99	
Fusion, 686.3/222.31	3.087	
222.31-237.75°K., graphical	0.958	
Vaporization, 47241237.75	19.87	
Entropy at the boiling point.	47.8	± 0.1 E. U.

There are practically no data for use in making a correction for gas imperfection at the boiling point. We will, however, assume a very uncertain additive correction of 0.1 E. U., as was done in the case of hydrogen chloride and hydrogen bromide.

The Entropy of Hydrogen Iodide from Spectroscopic Data.—The only measurements on the rotational states of hydrogen iodide are those of Czerny,[15] who obtained only four lines of the pure rotation band. These are sufficient to determine the moment of inertia with some accuracy but are hardly enough to justify a calculation of the entropy from the individual energy states, as was possible with hydrogen chloride and hydrogen bromide, although Czerny gives a formula which could be used for extrapolation. However, for the case of a polar diamagnetic gas, we may use the approximate formula for rotational entropy obtained by Sackur and Tetrode, namely, $S_R = R + R$ In $8\pi^2IT/h^2$, where I represents the moment of inertia of the molecule and h is Planck's constant. This value added to the translational entropy obtained from the Sackur equation should give a theoretical value for the entropy which is sufficiently accurate for comparison with our calorimetric value.

---

[15] Czerny, (a) Z. *Physik*, 44, 235 (1927); (b)45, 476 (1927).

The value obtained for the entropy of ideal hydrogen iodide gas at the temperature of the boiling point and a pressure of one atmosphere is **47.8** or **47.5** cal. per degree per mole, corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. The results are given in Table VIII, which also summarizes the results for the other halogen acids.

TABLE VIII

COMPARISON OF SPECTROSCOPIC AND THIRD-LAW VALUES OF THE ENTROPY OF THE HYDROGEN HALIDES

		Spectroscopic		Third law	
	T, ° K.	Tetrode const.	Lewis const.	Actual gas	Corr. to ideal state
Hydrogen chloride	188.07	41.47	41.15	41.2 ± 0.1	41.3
	298.1	44.64	44.32	....	44.5
Hydrogen bromide	206.38	44.92	44.60	44.9 ± 0.1	45.0
	298.1	47.48	47.16	....	47.6
Hydrogen iodide	237.75	47.8	47.5	47.8 ± 0.1	47.9
	298.1	49.4	49.1	....	49.5

Table VIII contains two minor corrections to our previously published spectroscopic values. The value for hydrogen chloride at its boiling point has been increased by **0.03** E. U. The value for hydrogen bromide at 298.1°K. has been lowered by **0.05** E. U. Both these corrections are due to the detection of arithmetical errors in our previous calculations. The theoretical calculations should be accurate to **0.01** E. U.

In obtaining the third law value given for hydrogen iodide at **298.1**°K. (25°), it was assumed that $C_p = 7/2R$ between **237.75** and 298.1°K. This assumption is justified by the nearly complete absence of vibrational energy, as may be shown from the molecular vibrational frequency as estimated by Czerny.[15]

According to Redlich[16] the value of the chemical constant of hydrogen iodide obtained by Eucken, Karwat and Fried[17] leads to a value of **50.69** cal. per degree per mole for this substance. Eucken, Karwat and Fried had placed the error at ±0.7 E. U.

Our measurements support the Tetrode constant for the Sackur equation and also indicate that the third law of thermodynamics is, in fact, an exact law.

We express our thanks to Dr. H. L. Johnston for assistance in making the measurements on hydrogen iodide and to Prof. R. T. Birge for discussions of the spectroscopic data.

Summary

The heat capacity of solid and of liquid hydrogen iodide has been measured from **15.3**°K. to its boiling point.

---

[16] Redlich, "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, iibersetzt von Redlich, Julius Springer, Wien, 1927.

[17] Eucken, Karwat and Fried, Z. *Physik,* 29, **1 (1924).**

The melting point was found to be 222.31 ± 0.05°K.; the boiling point, 237.75 ± 0.05°K.

The heat of fusion is 686.3 ± 0.8 cal. per mole. The heat of vaporization at the boiling point is 4724 ± 5 cal. per mole.

Two regions of high heat capacity were found in the solid state which appear to be internal transitions of the molecule; however, one of these, in particular, after progressing over a considerable temperature range, seems to develop into the ordinary or sharp transition type.

The entropy has been calculated from the experimental data and the third law of thermodynamics.

The entropy has also been calculated from spectroscopic data. The two methods lead to the same value within the limit of our experimental error, thus supporting the validity of each method.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VI. OXIDATION OF HYDROGEN PEROXIDE BY CERIC SULFATE. INDIRECT DETERMINATION OF LEAD

BY N. HOWELL FURMAN AND JOHN H. WALLACE, JR.

RECEIVED JANUARY 21, 1929 PUBLISHED MAY 6, 1929

Introduction

Some of the uses of ceric sulfate in volumetric analysis have been described in other papers of this series[1] and in those of other investigators.[2] Von Knorre[3] made use of the reaction

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2$$

in the determination of cerium. He added an excess of hydrogen peroxide (freshly standardized) to the ceric solution and determined the excess of the former with 0.1 N permanganate solution. Atanasiu and Stefanescu have published data for a single potentiometric titration of hydrogen peroxide with ceric sulfate in sulfuric acid solution. Our observations have been made with various acids and with a variety of different concentrations of acid.

Experimental

The apparatus was similar to that described in previous papers of this series; a bright platinum wire and a N calomel electrode made up the electrode system.

---

[1] N. H. Furman, THIS JOURNAL, 50, 755, 1675 (1928); Furman and Evans, *ibid.*, 51, 1128 (1929).

[2] H. H. Willard and Philena Young, *ibid.*, 50, 1322, 1334, 1368, 1372, 1379 (1928); 51, 139, 149 (1929); *Ind. Eng. Chem.*, 20, 972 (1928); I. A. Atanasiu, *Bull. soc. roum. chim.*, 30, *1* (1928); Atanasiu and V. Stefanescu, Ber., 61, 1343 (1928); H. Rathsberg, *ibid.*, 61, 1664 (1928).

[3] V. Knorre, *Z. angew. Chem.*, 10, 685, 717 (1897); *Ber.*, 33, 1924 (1900).

The ceric sulfate solutions were prepared in two ways: (1) by dissolving commercial rare earth oxides in enough dilute sulfuric acid to make the resulting solution about 2–3 N in sulfuric acid when 0.1 N in oxidizing power; (2) by heating purified oxide (basic nitrate method) with an excess of sulfuric acid at approximately 200°. An appreciable portion of the oxide was unattacked. The resulting solution was approximately 0.1 N in oxidizing power and from 1.0-1.5 N in sulfuric acid. Both solutions were stable.

The solutions were standardized potentiometrically against pure sodium oxalate in hydrochloric acid solution of the concentration suggested by Willard and Young.[4]

Hydrogen peroxide solutions approximately 0.1 *N* were prepared by diluting pure 30% hydrogen peroxide (Merck's "Superoxol"). The solutions were kept in a smooth bottle of amber-colored glass, and were found to be stable for at least four hours. The normality of the hydrogen peroxide was determined by titration with potassium permanganate solution which had been standardized against sodium oxalate. All of the end-points were determined potentiometrically.

Titration of Hydrogen Peroxide with Ceric Sulfate.—Ten or 25 cc. of hydrogen peroxide were pipetted out and were generally diluted to 100 cc. after addition of acid. The nature and concentration of acid were found to be important factors; variations in initial volume or in rate of addition of ceric sulfate were minor factors. The titrations were made at room temperature. The results are summarized in the following table.

TABLE I

TITRATION OF APPROXIMATELY 0.1 N HYDROGEN PEROXIDE WITH CERIC SULFATE

A. In Hydrochloric Acid Solution

	1	2	3	4	5	6	7
Init. acid concn., N	2.5	2.5	2.5	1.7	0.5	5	2.5
Hydrogen perox., cc.	25	25	25	25	10	10	25
Ce(SO$_4$)$_2$ soln. Calcd., cc.	27.27	27.27	27.27	27.27	10.91	10.91	34.72
Found, cc.	27.26	27.31	27.30	27.28	10.89	10.90	34.70
Error in cc.	-0.01	+0.04	+0.03	$0.01	-0.02	-0.01	-0.02

B. In Sulfuric Acid Solution

	8	9	10	11	12	13
Initial acid concn., N	0.5	1.0	2	2	2	9
Hydrogen peroxide, cc.	25	10	25	25	25	25
Ce(SO$_4$)$_2$ soln. Calcd., cc.	35.58	10.91	35.58	35.58	34.72	34.72
Found, cc.	35.57	10.89	35.60	35.60	34.75	34.71
Error in cc.	-0.01	−0.02	+0.02	+0.02	+0.03	-0.01

	C. Acetic Acid		D. Nitric Acid	
	14	15	16	17
Initial concn. of acid, N	1	3	0.5	2
Hydrogen peroxide, cc.	10	10	10	25
Ce(SO$_4$)$_2$ soln. Calcd., cc.	10.91	10.91	10.91	27.27
Found, cc.	10.86	10.91	10.88	27.21
Error in cc.	-0.05	±0.00	-0.03	-0.06

Determinations 1–6, 9 and 14–17 were made with 0.0991 N ceric sulfate which was prepared from commercial rare earth oxides. In the other instances the ceric solution, prepared from the purified oxide, was 0.0760 N.

---

[4] Willard and Young, THIS JOURNAL, 50, 1327 (1928).

The character of the titration graphs is indicated in Pig. 1. The downward trend just before the end-point that is shown in Curve 2 is usually a characteristic of titrations in hydrochloric acid solution.

When the initial concentration of sulfuric acid is below 1 N, the rate of reaction is very small, and the break in potential at the end-point is usually below 0.1 volt. The reaction was very sluggish at all of the concentrations of sulfuric acid that were used. From three to five minutes are required for the potential to become steady near the end-point. The voltage rise at the end varies from 0.15 to 0.25 volt per 0.05 cc. of ceric solution as the concentration of acid is increased.

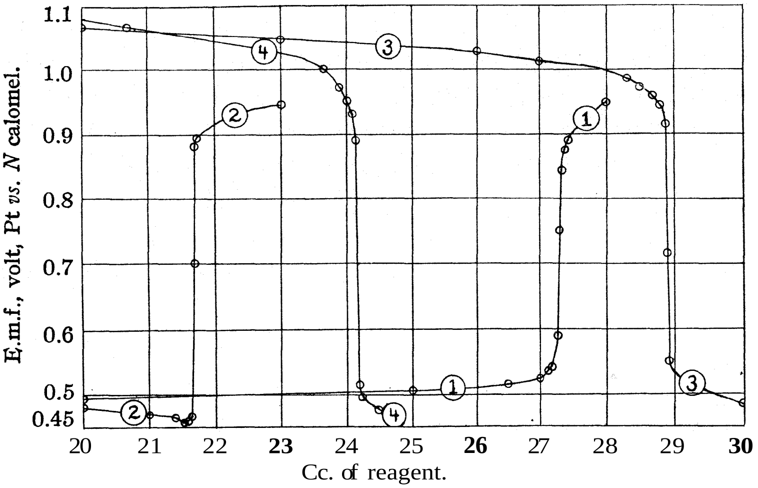


Fig. 1.—Curve 1. Titration of hydrogen peroxide in sulfuric acid solution (3.6 *N*). Curve 2. Titration of hydrogen peroxide in 1.2 *N* HCl solution. In 1 and 2 the ceric sulfate was 0.1051 *N*. Curve 3. Titration of 25 cc. (0.1051 N) ceric sulfate with peroxide. Initial acid concentration, 2.5 *N* (H_2SO_4). Curve 4. Titration of 25 cc. of 0.0991 N ceric sulfate with peroxide. Original acid concentration, 0.7 N.

The reaction proceeds very rapidly at all of the concentrations of hydrochloric acid that were tested. The rise in e.m.f. at the end-point is very sharp, and is of the order of 0.25–0.32 volt per 0.05 cc. of 0.1 N ceric solution. Acetic acid solutions give an equally rapid reaction rate and about the same rise in voltage at the end-point. When nitric acid is present the rise in voltage per drop of ceric solution is less, being of the order of 0.2–0.25 volt. The rate of reaction is somewhat slower than with hydrochloric acid.

The visual end-point was noted in a number of instances. In general it is 0.05 cc. beyond the potentiometric end-point. The presence of iron (about 1 mg. per 25 cc.) in the ceric solution obscures the end-point in solutions that contain high concentrations of hydrochloric acid.

The Reverse Titration.—The procedure was similar to that which has been described. The nature of the results is indicated in the following table.

TABLE II

TITRATION OF 0.0991 *N* CERIC SULFATE WITH 0.1027 *N* HYDROGEN PEROXIDE

Acid added		None	None	H_2SO_4	HNO_3	HNO_3	H_2SO_4
Initial concn., N		....	....	3	1.5	1.5	5
Ceric sulfate, cc.		25	25	25	25	25	10
H_2O_2, cc.	Calcd.	24.12	24.12	24.12	24.12	24.12	9.64
	Found	24.09	24.11	24.09	24.12	24.12	9.65
Error, cc.		−0.03	−0.01	−0.03	±0.00	±0.00	+0.01

When no acid was added the break in potential was about 0.4 volt per drop of hydrogen peroxide solution, and in the other instances it was about 0.2 volt per 0.05 cc. at the end-point. The nature of the graph is shown by Curves 3 and 4, Fig. 1.

Indirect Determination of Lead Peroxide

A determination of lead peroxide has been based upon the fact that an excess of hydrogen peroxide reacts with lead peroxide in nitric acid solution. The excess of hydrogen peroxide is then determined with permanganate.[5]

Our results showed that ceric sulfate could be employed to determine the excess of hydrogen peroxide.

Weighed samples of minium, ranging between 0.18 and 0.25 g., were transferred to a mixture of 25 cc. of approximately 0.1 N hydrogen peroxide (standardized against ceric sulfate) and 25 cc. of concentrated nitric acid of sp. gr. 1.42 (free from dissolved oxides of nitrogen). Solution of the lead oxide was complete after a few minutes' stirring. The excess of hydrogen peroxide was determined. The weight of PbO_2 was calculated from the amount of hydrogen peroxide that had been decomposed. The values which one of us (F) had obtained by Bunsen's iodometric method were unknown to the other (W) until after the determinations with ceric sulfate had been completed.

No. 1	Found, using $Ce(SO_4)_2$	33.71, 33.61, 33.95% of PbO_2
	Found, iodometrically	33.70, 33.89, 33.81, 33.65% of PbO_2
No. 2	Found, using $Ce(SO_4)_2$	25.68, 25.58, 25.61, 25.65, 25.81% of PbO_2
	Found, iodometrically	25.80, 25.73, 25.65% of PbO_2

After the end of a titration there was usually a slight precipitate of lead sulfate which did not interfere in any way with the convenience of the method.

The hydrogen peroxide–ceric sulfate procedure was not reliable in the determination of manganese dioxide in pyrolusite. The errors were in

---

[5] Schlossberg, *Z. anal. Chem.*, **41**, **743** (1902).

the direction that would be expected on the basis of catalytic decomposition of hydrogen peroxide during the slow process of dissolving the mineral.

Summary

The direct potentiometric titration of hydrogen peroxide with ceric sulfate has been shown to be accurate in solutions moderately acidified with hydrochloric, sulfuric, nitric or acetic acid. The reverse titration is also accurate in sulfuric and nitric acid solutions.

The hydrogen peroxide–ceric sulfate reaction may be applied in the indirect determination of lead peroxide.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. VI. REACTIONS WITH ORGANIC COMPOUNDS

BY R. W. BORGESON[1] AND J. A. WILKINSON

RECEIVED FEBRUARY 8, 1929 PUBLISHED MAY 6, 1929

Hydrogen sulfide has been found by different workers to be a good solvent for organic substances[2] and for this reason it was thought important to study the reactions between liquid hydrogen sulfide and members of the different types of organic compounds.

Experimental

Several examples of each of the types of organic compounds were placed in glass tubes of 50-cc. capacity and, after cooling to $-77°$ with a mixture of ether and solid carbon dioxide, liquid hydrogen sulfide was added. The tubes were then sealed and allowed to come to room temperature. After standing for several weeks they were again cooled, opened, the excess of hydrogen sulfide was allowed to evaporate and the residues were examined for evidence of reaction.

The following types of organic compounds were studied: saturated hydrocarbons, unsaturated hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, alkyl and aryl halides, acids, acid anhydrides, esters, sugars, nitro compounds, Grignard reagent, amides, amines and acyl halides.

Hydrocarbons.—Benzene, toluene, naphthalene, anthracene, gasoline, kerosene and vaseline are all soluble and non-reactive in liquid hydrogen sulfide. The unsatu-

---

[1] This paper is from a portion of the work presented to the Graduate Faculty of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] McIntosh and Steele, *Proc. Roy. Soc. London,* 73, *450* (1904); Archibald and McIntosh, *ibid.,* **73,** 454 (1904); Antony and Magri, *Gazz. chim. ital.,* **75,** 206 (1905); Steele, McIntosh and Archibald, *Phil. Trans. Roy. Soc.,* **205A,** 99 (1906); Magri, *Atti. accad. Lincei, (V)16,* 171 (1907); Quam, THIS JOURNAL, **47,** 103 (1925); Quam and Wilkinson, ibid., **47,** 989 (1925); Kalston and Wilkinson, *ibid* , **50,** 258 (1928).

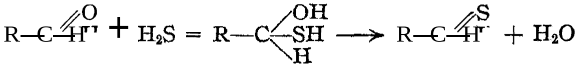
rated hydrocarbons amylene and trimethylethylene are miscible in liquid hydrogen sulfide but do not react with it unless the temperature is raised to room temperature and even then the reaction is a slow one. If after standing at room temperature for several weeks the tubes are again cooled to −77°, a white solid separates out which has a strong mercaptan odor. This solid decomposes and disappears on bringing it to room temperature. Since neither amylene nor trimethylethylene is a solid at −77, the formation of a solid is evidence that a reaction has taken place. Probably this is an addition reaction at the double bond, but no analytical data could be obtained because of the instability of the compounds.

Alcohols.—Methyl, ethyl, *iso*butyl, and *iso*-amyl alcohols and glycerin are miscible in liquid hydrogen sulfide at −77°, while allyl and furyl alcohols are miscible at room temperature. After standing for two months, the first three of these gave a precipitate of sulfur on cooling, showing that some decomposition had taken place. The allyl alcohol gave a small amount of a viscid liquid that had a strong mercaptan odor, which would indicate that an addition product had formed at the double bond.

Phenols.—Phenol, cresol, and m-aminophenol are soluble in liquid hydrogen sulfide, the latter but slightly, however; none of them gave any indication of reaction.

Ethers.—Ethyl ether, the only one tried, is miscible but non-reactive in liquid hydrogen sulfide.

Aldehydes.—Acetaldehyde, butylaldehyde, acrylaldehyde, benzaldehyde, m-nitrobenzaldehyde, trinitrobenzaldehyde, p-tolualdehyde, cinnamaldehyde and furfuraldehyde all dissolve in liquid hydrogen sulfide and react with it. In every case after standing for several days a second liquid layer formed and if the tube was again cooled white crystals of the compound $H_2S \cdot xH_2O$ were formed. This reaction took place with every aldehyde studied and was accompanied by the development of the odor of a mercaptan. With benzaldehyde, p-tolualdehyde, cinnamaldehyde and furfuraldehyde the reaction was carried to such an extent that after driving off the excess of hydrogen sulfide and bringing to room temperature a gelatinous mass remained. In the case of furfuraldehyde this was purified by recrystallizing from ethyl acetate and found to be furfural thioaldehyde, C_4H_3OCSH.[3] The reaction must consist of the addition of hydrogen sulfide to the aldehyde and then dehydration of the resulting compound.



$$\mathrm{R{-}C{\overset{\displaystyle O}{\diagup\!\!\diagup}}H} + H_2S = \mathrm{R{-}C}\begin{matrix}\diagup OH\\ -SH\\ \diagdown H\end{matrix} \longrightarrow \mathrm{R{-}C{\overset{\displaystyle S}{\diagup\!\!\diagup}}H} + H_2O$$

Ketones.—Acetone, diethyl ketone, acetyl ketone, acetophenone and benzophenone were all soluble in liquid hydrogen sulfide and, while the last two showed no evidence of reaction, the first three developed a small amount of pink color and a mercaptan odor.

Alkyl and **Aryl** Halides.—Ethyl chloride, bromide and iodide, methyl iodide, *iso*-butyl bromide, n-propyl iodide, *n*-butyl iodide, benzyl chloride, benzyl iodide, allyl bromide and iodide were all soluble in liquid hydrogen sulfide and, with the exception of the allyl halides, all were non-reactive. These latter reacted because of the presence of the double bond.

Acids.—A number of organic acids such as acetic, propionic, benzoic and cinnamic were found to be soluble but non-reactive except the last, which contains a double bond.

Acid Anhydrides.—Acetic, benzoic, succinic and malic acid anhydrides were soluble in liquid hydrogen sulfide, the latter being but slightly so. There was no evidence of reaction except a slight decomposition of the hydrogen sulfide giving free sulfur.

Esters.—Ralston and Wilkinson[4] have shown that esters are soluble in liquid hydrogen sulfide and are thiohydrolyzed just as they are hydrolyzed in water.

---

[3] Meints and Wilkinson, THIS JOURNAL, 51, **803** (1929).

[4] Ralston and Wilkinson, *ibid.*, 50, 2160 (1928).

Salts.—Most metal salts of organic acids are insoluble in liquid hydrogen sulfide.

Sugars.—Sucrose, glucose, maltose, lactose, mannose, arabinose and raffinose are insoluble in liquid hydrogen sulfide and show no evidence of reacting with it.

Grignard Reagents.—Ethylmagnesium bromide, phenylmagnesium bromide and benzylmagnesium chloride, either solid or dissolved in ether, all react vigorously with liquid hydrogen sulfide giving the corresponding hydrocarbon and a white solid suspended in the liquid. This solid, on evaporating the liquid slowly, gives off hydrogen sulfide and takes up water from the air readily. A study of the products of this reaction is being made.

Amides.—Acetamide, n-butyramide, acetanilide, benzanilide and phthalimide are all soluble but give no evidence of reaction. Picramide reacts slowly, liberating sulfur due to the presence of the nitro group.

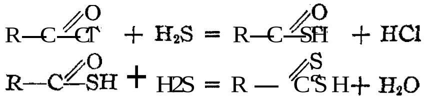
Amines.—Diethylamine, *sec.*-butylamine, *iso*butylamine and di-n-butylamine all react with liquid hydrogen sulfide and form either viscid liquids or crystalline solids which decompose readily, giving off hydrogen sulfide.

Dimethylaniline, diethylaniline, diphenylamine, a-naphthylamine, β-naphthylamine and benzidine are soluble but do not react with liquid hydrogen sulfide. Aniline and benzylaniline react similarly to the alkylamines, forming white crystalline compounds which decompose rapidly, giving off hydrogen sulfide and forming a red liquid which slowly decomposes. Phenylhydrazine reacts with liquid hydrogen sulfide to form yellow-white crystals of the compound $C_6H_5NHNH_2{\cdot}H_2S$. After evaporating off the hydrogen sulfide a red liquid is obtained which slowly gives off ammonia, deposits sulfur and leaves liquid aniline according to the equation

$$C_6H_5NHNH_2 + H_2S = C_6H_5NHNH_2{\cdot}H_2S = C_6H_5NH_2 + NH_3 + S$$

The red liquid is an intermediate product between the addition compound and aniline. This breaks down very slowly on standing and more rapidly if shaken vigorously. A similar red solution is obtained when phenylhydrazine is saturated with hydrogen sulfide gas. The odor of ammonia is not then perceptible until the mixture has stood for three or four days.

Acyl Halides.—All of the acyl halides studied dissolve in liquid hydrogen sulfide and react with it more or less readily. This corresponds to the reaction with water to form the acid. In addition a second reaction takes place whereby the oxygen of the halide is replaced by sulfur, forming the dithio-acid.



$$R{-}C\overset{/\!\!/O}{-}Cl + H_2S = R{-}C\overset{/\!\!/O}{-}SH + HCl$$

$$R{-}C\overset{/\!\!/O}{-}SH + H_2S = R - C\overset{/\!\!/S}{-}SH + H_2O$$

Benzyl chloride and bromide, α-bromopropionyl bromide, phthalic chloride, succinyl chloride, benzenesulfonyl chloride and phenylacetyl chloride all reacted and gave varying amounts of yellow to red liquids containing the dithio acids.

Acetyl chloride and acetyl bromide both reacted readily with liquid hydrogen sulfide, forming a deep orange-colored liquid. When the tubes were opened and the hydrogen sulfide pressure thus reduced, fine white crystals were formed mingled with the red liquid. These were purified by recrystallizing from ether.

Anal. Calcd. for $(CH_3CS)_2S$: S, 64.01; C, 31.97; H, 4.02. Found: S, 63.98. 63.84; C, 32.27, 32.6; H, 4.14, 4.12.

This would show that the compound is the anhydride of dithioacetic acid. This compound has not been prepared before. The following are the properties observed: melting point, 225°; readily soluble in acetone, benzene, carbon disulfide, chloroform, carbon tetrachloride and ethyl acetate. It is fairly soluble in ether, petroleum ether and hot alcohol. Cold solutions of aniline and the amines dissolve it. It is insoluble in water, dilute acids or alkalies and inorganic solvents in general. Molecular weight determinations by the freezing point lowering method, when dissolved in benzene, gave values of 269, 270 and 272, which show that it is somewhat associated in benzene solution since the simple formula for $(CH_3CS)_2S$ has a molecular weight of but 150.

Conclusions

1. The solubilities of the different types of organic compounds in liquid hydrogen sulfide have been observed.
2. The presence of a double bond in the organic compound is usually shown by the development of the odor of a mercaptan.
3. The aldehydes, amines and acyl halides are the only types that show much evidence of reacting with the liquid hydrogen sulfide.
4. The amines give unstable addition products with hydrogen sulfide.
5. The aldehydes tend to substitute a sulfur atom for the sulfur of the aldehyde group to form a thio-aldehyde.
6. The acyl halides tend to substitute an SH group for the halide and an S for the oxygen and form dithio acids to a small amount. Acetyl chloride and bromide form the dithioacetic acid, which then loses hydrogen sulfide and forms the thioanhydride.

AMES, IOWA

NOTES

A Sensitive Test for Magnesium.[1,2]—K. Suitsu and K. Okuma[3] state that the azo dye, *o,p*-dihydroxy-azo-*p*-nitrobenzene gives a very sensitive test for the magnesium ion. This reagent has been used in the courses of qualitative analysis at this University for two years with excellent results. The authors claim to be able to detect $^1/_{500}$ mg. of magnesium by means of this test.

The dye is readily prepared by diazotizing *p*-nitraniline and coupling it with the theoretical quantity of resorcinol dissolved in dilute sodium hydroxide solution. The solution is acidified and the precipitated dye filtered off. The product may be purified by recrystallization from methyl alcohol as a dark red powder, m. p., 199–200°. A convenient concentration for ordinary use is a 0.5% solution of the dye in 1% sodium hydroxide. Some deterioration of the reagent occurs in solution after a year's standing.

The solution to be tested for magnesium is made slightly acid with dilute hydrochloric acid and one drop of the reagent added. On making

---

[1] Hahn, Ber., 57, 1394 (1924); 60, 975 (1927), describes a somewhat similar test for magnesium using 1,2,5,8-tetrahydroxy-anthraquinone.

[2] Since this note has been accepted for publication, the Eastman Kodak Company has informed me that they intend placing the reagent on the market.

[3] Suitsu and Okuma, *J. Soc. Chem. Ind. Japan*, 29, 132–138 (1926); *C. A.*, 20, 3000 (1926).

the solution alkaline with dilute sodium hydroxide, the characteristic sky-blue precipitate of the magnesium lake appears. If the amount of magnesium is very small, a drop of the stock reagent which has been diluted 4 to 5 times with water gives better results. In this case also the lake is rather slow in forming and shaking for two to three minutes is necessary to coagulate the precipitate.

Professor D. P. Smith of this University found that an excess of ammonium salts destroys the sensitivity of the reagent; hence in the regular course of analysis, the ammonium salts are "smoked off" in a casserole before applying the test.

Nickel and cobalt also give somewhat similar blue lakes which may lead to confusion. After the removal of the heavy metals by precipitation as sulfides, however, the test is absolutely characteristic and the confusion attending the use of the classical magnesium ammonium phosphate precipitate as a test, especially in elementary courses of analysis, is obviated.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

WM. L. RUIGH

RECEIVED NOVEMBER 14, 1928
PUBLISHED MAY 6, 1929

The Preparation of **Selenic** Acid and its Salts.—A number of methods for the preparation of selenic acid have been reported in the literature.[1] As a rule the salts of this acid have been prepared by the oxidation of the selenites.

Meyer and Heider[1a] treated selenium dioxide with 30% hydrogen peroxide, warming the mixture on the water-bath and upon analysis found that 48% of the oxide had been oxidized to selenic acid. In another experiment using a larger amount of hydrogen peroxide an analysis showed an oxidation of 70%.

The experiments of Meyer and Heider suggested that it might be worth while to try to find the best conditions for preparing selenic acid, and possibly the selenates, by the hydrogen peroxide method.

A number of experiments were carried out, treating weighed amounts of selenium dioxide with varying amounts of hydrogen peroxide. The time and the temperature of the treatment were varied. Oxidation values all the way from 20 to 70% were obtained. Small amounts of the oxide

---

[1] The methods for the preparation of selenic acid and its salts are found in the following references: (a) Meyer and Heider, *Ber.*, 48, 1154 (1915); (b) Mitscherlich, *Pogg. Ann.*, 9, 623 (1827); (c) Wohlwill, *Ann.*, 114, 169 (1860); (d) *Wien Akad. Ber.*, 39, 299 (1860); (e) Thomsen, *Ber.*, 2, 598 (1869); (f) Diemer and Lenher, *J. Phys. Chem.*, 13, 505 (1909); (g) Mdller, *Ber.*, 36, 4262 (1903); (h) *Chem.-Ztg.*, 31, 630 (1907); (i) Meyer and Moldenhauer, *Z. anorg. Chem.*, 116, 193 (1921); (j) Worsley and Baker, *J. Chem. Soc.*, 123, 2870 (1923).

were then refluxed with 30% hydrogen peroxide, with the result that the oxidation values were much higher. These results were reproducible as is shown in the following table.

TABLE I

RESULTS OF EXPERIMENTS

Selenium dioxide, g.	0.2019	0.2000	0.2029
Hydrogen peroxide, 30%, cc.	10	10	10
Time of refluxing, hours	2	2	2
Oxidation, %	89.5	90.7	91.9

A quantity of selenic acid was prepared, adhering to the conditions shown in Table I, The small amount of selenious acid was reduced to selenium, filtered off and the filtrate concentrated, following the procedure of Cameron and Macallan.[2] In this manner selenic acid of high purity with a concentration of 84% was readily prepared.

Since hydrogen peroxide proved so effective in oxidizing selenious acid, it seemed desirable to try its use for the oxidation of selenites to selenates. Copper selenite was prepared by treating copper carbonate with selenious acid. The green, insoluble copper selenite remained. This salt was covered with 30% hydrogen peroxide and refluxed for three hours, during which time it was oxidized to the blue, soluble selenate. A small amount of the insoluble selenite was filtered off, leaving a clear blue filtrate from which copper selenate crystals formed, identical in appearance to those of copper sulfate. Using the same procedure selenates of nickel, cobalt, aluminum and magnesium were prepared. All of these salts were obtained in a well defined, crystalline condition, similar to the corresponding sulfates.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK

ERNEST R. HUFF
C. R. MCCROSKY

RECEIVED NOVEMBER 23, 1928
PUBLISHED MAY 6, 1929

Use of Cresol Red in Acid Solutions.—As has been pointed out by Clark[1] and Cohen,[2] the sulfonephthalein indicator dyes undergo two distinct color changes at different points on the PH scale. However, of this series only thymol blue and meta cresol purple have been applied as indicators in both acid and alkaline solutions and the fact that the sulfonic acid dissociation of cresol red is sufficiently repressed so that it can be used in acid solutions has not been emphasized. This indicator is really

---

[2] Cameron and Macallan, Chem. *News*, 59, 219 (1899).

[1] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1922, p. 93.

[2] Cohen, "U. S. Public Health Reports," 41, 3051-3074 (1926).

quite valuable in certain cases. The color change is from red at PH 0.2 to yellow at PH 1.8, the half transformation point occurring at a hydrogen-ion concentration of approximately 1.0×10^{-1}, or PH 1.0. The virage resembles those of thymol blue and meta cresol purple over their acid ranges.

Cresol red can be used to advantage in testing for free mineral acids in solutions of weak acids, such as citric or acetic, or hydrolyzable salts of an acidic nature, such as ferric chloride or sulfate. It can also be employed in adjusting solutions in qualitative analysis, so as to separate the sulfides of the second and third groups. Cresol red is superior to methyl violet in that it is quite stable in solution and also gives stable, reproducible colors.

CONTRIBUTION FROM THE
RESEARCH LABORATORY
LAMOTTE CHEMICAL PRODUCTS CO.
BALTIMORE, MARYLAND

F. R. MCCRUMB
W. R. KENNY

RECEIVED JANUARY 7, 1929
PUBLISHED MAY 6, 1929

The Rapid Concentration of Germanium and Gallium Contained in Zinc Oxide Carrying Them.—The method usually given for the extraction of germanium and gallium from zinc oxide carrying a small percentage of these elements, calls for solution in hydrochloric acid and the subjection of the whole solution to distillation, after oxidizing the arsenic with potassium chlorate or other suitable oxidizing agent. It has been found in the Laboratories of the University of New Hampshire that the two elements can be rapidly concentrated as follows.

The zinc oxide was dissolved in an excess of commercial hydrochloric. acid, allowed to stand for a short time and the precipitate of lead chloride removed by filtration. The hot solution, while being thoroughly stirred, was then rendered basic by the slow addition of some of the original zinc oxide. After continuing the stirring for some time to make certain of the precipitation of all the germanium and gallium, the precipitate carrying them was filtered off, dissolved in hydrochloric acid, distilled and treated in the usual manner to obtain the two elements.

In order to ascertain the completeness of their precipitation by the treatment with zinc oxide, large portions of the filtrates from several different runs were strongly acidified with hydrochloric acid, the arsenic was oxidized with potassium chlorate, a portion distilled off and hydrogen sulfide passed into the distillate. The absence of any germanium sulfide was considered evidence that all but negligible quantities at least of that element had been removed. The liquid remaining in the flask after distillation was examined by means of the spark spectrum for gallium after any traces of it had been concentrated by neutralizing with ammonum hydroxide and rendering basic with metallic zinc, etc. The violet lines characteristic of it were not visible.

By employing this preliminary concentration 100 lb. of zinc oxide could be put through the distillation process in four or five runs using a 12-liter Pyrex flask, whereas before this method was used it required 25 to 30 runs; also, the quantity of material from that process which had to be worked over for gallium was correspondingly decreased.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

C. JAMES
H. C. FOGG

RECEIVED JANUARY 9, 1929
PUBLISHED MAY 6, 1929

Determination of Ethylene by Absorption in a Solution of Silver Nitrate.—During the course of a study of the catalytic hydrogenation of acetylene[1] the author observed that a solution of silver nitrate is capable of absorbing ethylene. A preliminary test at that time tended to indicate that the reaction might be used for the quantitative determination of the latter gas.

A search of the literature revealed that reactions between ethylene and silver salts have been previously observed by Ross and Trumbull,[2] Gluud and Schneider[3] and Lommel and Engelhardt.[4] The feasibility of using a solution of a silver salt alone as an absorbing medium in the determination of ethylene has apparently never been investigated.

Reactions between ethylene and salts of a few other metals have also been observed. In this connection, attention may be directed to the suggestion[5] for the use of a solution of mercuric nitrate over mercury as a quantitative absorbing agent for this gas.

The apparatus used during a brief investigation of the usefulness of a solution of silver nitrate as an absorbent in the determination of ethylene has been described previously by the author.[6] In its use the absorbing solution is passed slowly over and around the gaseous sample and is removed continuously at the bottom. Such an apparatus is particularly advantageous in cases where, as appeared to be probable in this case, there is a tendency toward an equilibrium condition involving incomplete absorption.

The table below records the results of a comparison of the absorption of ethylene from a mixture consisting essentially of nitrogen and ethylene by solutions of silver nitrate of various concentrations. The volumes of

---

[1] Morris and Reyerson, *J. Phys. Chem.*, 31, 1332 (1927).

[2] Ross and Trumbull, THIS JOURNAL, 41, 1180 (1919).

[3] Gluud and Schneider, *Ber.*, **57B, 254** (1924).

[4] Lommel and Engelhardt, *ibid.*, **57B,** 848 (1924).

[5] See Treadwell–Hall, "Quantitative Analysis," 7th ed., John Wiley and Sons, Inc., New York, p. 698.

[6] Morris, THIS JOURNAL, 49 979 (1927).

solutions and the time requirements shown, while not necessarily representing the exact minima in every case, do give indication of what may be expected in a satisfactory operation carried out as rapidly as a careful observation of the progress of the absorption appears to justify.

TABLE I

THE ABSORPTION OF ETHYLENE BY SOLUTIONS OF SILVER NITRATE

Concn. of soln., %	40	20	10	5
Vol. of soln. used, cc.	12	28	40	80
Time for absorption, sec.	55	75	180	240
Red. in vol. of 50 cc. sample, cc.	34.8	34.9	34.9	34.7

The absorption by the more concentrated solutions was more rapid. The use of concentrated solutions is also recommended as a consequence of the fact that the completion of absorption can be more readily judged when using them rather than the slower absorbing dilute solutions.

In an additional experiment a comparison was made between a solution of silver nitrate and other reagents commonly used in the quantitative absorption of ethylene. The value for the ethylene content of a mixture of this gas with nitrogen as indicated by absorption with fuming sulfuric acid agreed closely with that obtained on the same mixture when a 20% solution of silver nitrate was used. The fact that absorption by bromine gave a slightly different value was attributed to a change in the composition of the gaseous mixture during the time interval between tests.

There are certain advantages in the use of silver nitrate for this purpose. It is interesting to note, for instance, that, in accordance with the observation of Lommel and Engelhardt,[4] the ethylene may subsequently be removed from the solution by evacuation. Recovery of the absorbing solution is thus possible. Evaporation can readily be applied to restore it to the concentration desired for subsequent determinations. Whether heat alone would free the solution from ethylene as well as concentrate it remains to be investigated. A solution of silver nitrate has, moreover, a decided advantage over the commonly used absorbents, bromine and strong sulfuric acid, in that the chemical and physical properties of these latter make them anything but pleasant reagents to handle.

There are several points in connection with the reaction between ethylene and silver nitrate which seem to be worthy of further study. Of primary interest is the question of the composition and properties of the reaction product. The possibility of increasing the effectiveness of absorption by adding acids such as sulfuric or phosphoric to the solution of silver nitrate also merits investigation.* As a final consideration attention may be directed to the fact that acetylene may be determined by titration of the nitric acid released when this gas reacts with a solution of silver nitrate. The possibility of determining both acetylene and ethylene in a mixture of the two by the use of a single absorbing agent, a solution of silver nitrate, is at once apparent.

V. N. MORRIS[7]

RECEIVED JANUARY 12, 1929
PUBLISHED MAY 6, 1929

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHEMICAL DEPARTMENT OF THE CITY OF CHICAGO MUNICIPAL TUBERCULOSIS SANITARIUM]

MENTHOL STUDIES. II. MENTHYL ESTERS OF THE 2-NITRO-4-CARBOXYPHENYLARSONIC AND PHENYLARSENIOUS ACIDS

BY K. LUCILLE McCLUSKEY

RECEIVED OCTOBER 3, 1928 PUBLISHED MAY 6, 1929

The first report[1] on the synthesis of aromatic terpene compounds to be used in chemotherapeutic studies in experimental tuberculosis included menthyl esters of the nitro- and aminocinnamic acids. Due to the great insolubility in water caused by the menthol, the menthyl esters of the aminocinnamic acids could not be made water-soluble through their hydrochlorides. Since a water-soluble product is desirable, the introduction of arsenic into the aromatic terpene group was thought to be desirable for two reasons; first, to increase the solubility in water and second, to confer probably greater therapeutic properties.

A few organic arsenicals have been used in experimental studies in tuberculosis therapy, and arsenic in the form of arsenic acid was tried early in the treatment of tuberculosis. Sodium cacodylate, atoxyl, arsacetin and neosalvarsan have no tuberculocidal properties, according to Arkin and Corper,[2] but earlier investigators (Buchner, Weismayr, Pokhorow)[3] comment favorably upon the worth of arsenic in the treatment of tuberculosis because of its favorable influence on metabolism, although they conclude that it is not a true chemotherapeutic agent with a specific action on human tubercle bacilli. .

The new menthol arsenicals described here were made with the hope that they might possess some favorable pharmacological action.

Experimental

2-Nitro-4-methylphenylarsonic Acid.—This compound was first prepared by Jacobs, Heidelberger and Rolf[4] using a different technique in the arsonation process from that described here. 3-Nitro-4-toluidine (110 g.) is stirred by means of a mechanical stirrer in 20% hydrochloric acid (500 cc.) until the hydrochloride is formed, and then diazotized at 0° with sodium nitrite (55 g.) dissolved in water (250 cc.). The diazo solu-

---

[7] Present address—Firestone Tire and Rubber Company, Akron, Ohio.

[1] McCluskey and Sher, THIS JOURNAL, 49, 452 (1927).

[2] Arkin and Corper, J. *Infectious Diseases,* 18, 333 (1916).

[3] Quoted by Weismayr in Ott's, "Chem. Path. der Tuberc.," 1903, p. 480481.

[4] Jacobs, Heidelberger and Rolf, THIS JOURNAL, 40, 1585 (1918).

tion is filtered from a small amount of undissolved substance. Solutions of hydrated copper sulfate (25 g. in 375 cc. of water), sodium hypophosphite (35 g. in 500 cc. of water) and sodium arsenite (135 g. in 1 liter) are heated separately to 60 to 70°, and then poured into a large flask. At this temperature the cold filtered diazo solution is added slowly with vigorous stirring. Nitrogen is evolved copiously and in a short time a stormy reaction sets in and the arsonic acid is immediately precipitated Very little tarry material is formed. After the evolution of nitrogen has subsided the substance is collected and washed well with water; yield, 130 g. The arsonic acid is purified by solution in 4% potassium hydroxide, treatment with charcoal and precipitation with hydrochloric acid. Further purification from alcohol gives a substance melting in a closed tube at 253–255". It is insoluble in benzene and acetone, slightly soluble in hot ethyl alcohol and quite soluble in hot methyl alcohol.

Anal. Subs., 0.2082: 29.99 cc. of I_2 soln. (1 cc. = 0.001967 g. of As). Calcd. for $C_7H_8O_5NAs$: As, 28.74. Found: 28.34.

2-Nitro-4-carboxyphenylarsonic Acid.—Maschmann[5] prepared this compound through the oxidation of the corresponding methyl compound with potassium permanganate. A convenient method for the preparation in rather large quantities is as follows. Crude 2-nitro-4-methylphenylarsonic acid (390 g.) is dissolved in potassium hydroxide solution (390 g. in 7.5 liters of water) treated with charcoal and filtered. Mechanical stirring facilitates the process. To the clear filtrate is added a solution of potassium permanganate (390 g. in 12.5 liters of water) and the reaction mixture placed on a water-bath until the permanganate color is lost through oxidation. The manganese oxides are removed by filtration and the green colored filtrate is acidified with hydrochloric acid until acid to congo red. The green color changes to pink and finally disappears. The acid solution is evaporated to dryness on the water-bath and the desired arsonic acid extracted with hot ethyl alcohol. The alcohol is removed by evaporation and the nitrocarboxyphenylarsonic acid is purified by crystallization from boiling water after treatment with charcoal; yield, 80 to 90%. The glistening needle-like crystals contain one molecule of water of crystallization and melt with decomposition at 226–227°, which confirms Maschmann's findings.

Anal. Subs., 0.2484, 0.1987: 30.84, 24.67 cc. of I_2 (1 cc. = 0.001933 g. of As). Calcd. for $C_7H_6O_7NAs \cdot H_2O$: As, 24.27. Found: As, 24.01, 24.00.

The water of crystallization is lost at 115° and the following analysis is obtained.

Anal. Subs., 0.2126, 0.2030: 28.25, 26.93 cc. of I_2 soln. (1 cc. = 0.001967 g. of As). Calcd. for $C_7H_6O_7NAs$: As, 25.77. Found: As, 26.14, 26.10.

Sodium Salt.—This salt is prepared by titrating an alcoholic solution of 2-nitro-4-carboxyphenylarsonic acid with an alcoholic solution of sodium hydroxide. The sodium salt is very soluble in water.

Anal. Subs., 0.2076: 22.41 cc. of I_2 soln. (1 cc. = 0.001967 g. of As). Calcd. for $C_7H_3O_7NAsNa_3$: As, 21.01. Found: As, 21.23.

2-Nitro-4-carboxyphenyldichloro-arsine.—The phenyldichloro-arsine compound can be obtained by reduction of the corresponding arsonic acid in concentrated hydrochloric acid with either hypophosphorous acid, sulfur dioxide, hydroquinone or camelite. 2-Nitro-4-carboxyphenylarsonic acid (20 g.) is dissolved in concentrated hydrochloric acid (150 cc.) and after the addition of 10% potassium iodide (10 drops) sulfur dioxide is passed into the solution until precipitation is complete. The dichloro-arsine compound is collected under suction on hardened filter paper, washed first with concentrated hydrochloric acid and then with dilute hydrochloric acid. Partial drying is obtained

---

[5] Maschmann, *Ber.*, **57B**, 1759–1766 (1924).

by pressing the preparation on a porous plate, after which it is transferred to a vacuum desiccator and dried over sulfuric acid and sodium hydroxide sticks; amount of crude product, 20 g. For purification the crude dried material is dissolved in hot chloroform and precipitated by cooling. Twelve grams of a light yellow, fluffy product melting at 173–174° is obtained. Petroleum ether added to the filtrate gives an additional quantity of less pure material.

Anal. Subs., 0.1740: 21.80 cc. of I_2 soln. (1 cc. = 0.001936 g. of As). Calcd. for $C_7H_4O_4NAsCl_2$: As, 24.04. Found: As, 24.26.

To a solution of 2-nitro-4-carboxyphenylarsonic acid (10 g.) in concentrated hydrochloric acid (400 cc.), 50% hypophosphorous acid (20 cc.) and 10% potassium iodide (10 drops) are added. The reaction mixture is gradually warmed to 37–40° and shortly the solution becomes turbid, the iodine color gradually disappears and the dichloro-arsine separates. The precipitate is collected and treated as described above; yield of crude product, 9 g.

2-Nitro-4-carboxyphenyldihydroxyarsine (2-Nitro-4-carboxyphenylarsenious Acid).—This compound can be prepared either by the hydrolysis of the corresponding dichloro-arsine or by reduction of the corresponding arsonic acid in water by means of sulfur dioxide in presence of potassium iodide as catalyst.

2-Nitro-4-carboxyphenylarsonic acid (10 g.) is dissolved in hot water (225 cc.) and after the addition of 10% potassium iodide (20 drops) sulfur dioxide is passed into the solution until complete precipitation of the arsenious acid; yield, 7.5 g. or 85%. 2-Nitro-4-carboxyphenylarsenious acid is a light yellow substance which does not melt or decompose below 290°.

Anal. Subs., 0.1718: 24.19 cc. of I_2 soln. (1 cc. = 0.001936 g. of As). Calcd. for $C_7H_6O_6NAs$: As, 27.28. Found: 27.26.

2-Nitro-4-carboxyphenyldichloro-arsine (3 g.) is suspended in water (100 cc.) and the mixture shaken for an hour. A change in structure is visible. The dihydroxyarsine is collected and washed free from chlorides. The filtrate becomes strongly acid and silver chloride is precipitated upon the addition of silver nitrate.

Menthyl Ester of 2-Nitro-4-carboxyphenylarsenious Acid.—2-Nitro-4-carboxyphenyldichloro-arsine (42 g.) is refluxed with thionyl chloride (100 cc.) on a water-bath for one hour. Complete solution results after fifteen minutes. The excess of thionyl chloride is removed by distillation under reduced pressure. To the crude acid chloride, menthol (54.6 g.) is added and the reaction mass is heated under a reflux condenser on a water-bath for one to one and a half hours. The excess menthol is removed by distillation under reduced pressure (outside bath 140') and petroleum ether is added to the residue, which dissolves the menthyl ester and separates it from an insoluble, tarry by-product. The petroleum ether is removed by evaporation and the sticky semi-liquid mass is macerated with 4 *N* sodium carbonate, whereupon a semi-solid mass is obtained which is dissolved in ether and shaken with more 4 N sodium carbonate until the carbonate solution is chloride free, The ether solution is washed with water, dried over anhydrous sodium sulfate and evaporated to dryness. The sticky mass soon crystallizes on stirring. The amount obtained at this point is 50 g. which still contains a small amount of free menthol. This ester, like menthol, is very soluble in organic solvents and is separated only with difficulty from small amounts of menthol through fractional crystallization. The last traces of menthol were best removed by steam distillation. The menthyl ester is a light yellow, crystalline substance which does not have a sharp melting point but gradually evolves a gas above 100°.

Anal. Subs., 0.2882, 0.3060: 28.38, 29.92 cc. of I_2 soln. (1 cc. = 0.001843 g. of As). Calcd. for $C_{17}H_{24}O_6NAs$: As, 18.16. Found: As, 18.14, 18.02.

Menthyl Ester of 2-Nitro-4-carboxyphenylarsonic Acid.—The menthyl ester of this acid could not be made directly from the acid itself with thionyl chloride and menthol, as the thionyl chloride reduced the arsonic group. The menthyl ester of 2-nitro-4-carboxyphenylarseniousacid (10 g.) is dissolved in acetone (200 cc.) and 3% hydrogen peroxide (105 cc.) is added in small portions at room temperature. The heat of reaction raises the temperature to 27–29°. After reaction is complete and the temperature subsides, the solution is filtered if necessary and allowed to stand in an evaporating dish at room temperature. The solid which separates after the evaporation of the acetone is collected and sucked dry. The ester is a white, crystalline substance which decomposes at 210–211° and is soluble in alcohol and chloroform, not so soluble in ether when pure and insoluble in petroleum ether. Purification from chloroform and petroleum ether gave a product of the following analysis.

Anal. Subs., 0.3012: 28.46 cc. of I_2 soln. (1 cc. = 0.001843 g. of As). Calcd. for $C_{17}H_{24}O_7NAs$: As, 17.48. Found: As, 17.41.

Sodium Salt.—The pure menthyl ester of 2-nitro-4-carboxyphenylarsonic acid is dissolved in warm ethyl alcohol and titrated to the pink point of phenolphthalein with an ethyl alcoholic solution of sodium hydroxide. The salt begins to separate as soon as the alkali is added but comes down at first in a gummy form. The solvent is removed through slow evaporation in a warm place and the salt is obtained as a white, fluffy substance. It is suspended in ethyl alcohol and macerated well to remove any excess either of free acid or free alkali, then collected and washed with ether. Thus obtained, the salt crystallizes with 4 molecules of water of crystallization.

Anal. Subs., 0.3336: 24.42 cc. of I_2 soln. (1 cc. = 0.001843 g. of As). Calcd. for $C_{17}H_{22}O_7NAsNa_2 \cdot 4H_2O$: As, 13.76. Found: As, 13.50.

After drying at 110°, the following analysis is obtained.

Anal. Subs., 0.2863: 24.45 cc. of I_2 soln. (1 cc. = 0.001843 g. of As). Calcd. for $C_{17}H_{22}O_7NAsNa_2$: As, 15.85. Found: As, 15.72.

The hydrated salt is a pure white substance while the anhydrous form is a very light yellow. Both forms are very soluble in water.

Summary

The preparation of the following new compounds is reported: 2-nitro-4-carboxyphenyldichloro-arsine, 2-nitro-4-carboxyphenylarsenious acid, menthyl ester of 2-nitro-4-carboxyphenylarsenious acid, menthyl ester of 2-nitro-4-carboxyphenylarsonic acid, together with some of the sodium salts. The presence of the nitro and the carboxy groups favors the arsenious acid form rather than the arsenious oxide form.

CHICAGO, ILLINOIS

[Contribution from the Baker Laboratory of Chemistry, Cornell University]

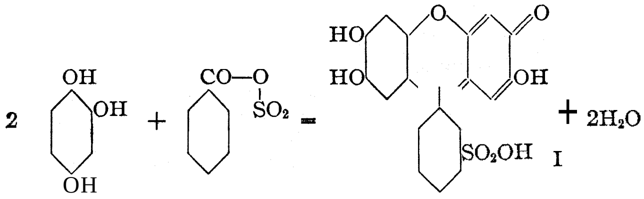
HYDROXYHYDROQUINOLSULFONEPHTHALEIN, 2',4',5'-TRIHYDROXYBENZOYLBENZENE-ORTHO-SULFONIC ACID (THE INTERMEDIATE ACID) AND SOME OF THEIR DERIVATIVES

By W. R. Orndorff and Mary L. Willard[1]

Received November 2, 1928 Published May 6, 1929

In 1900 Liebermann[2] and in 1901 Thiele and Jaeger[3] prepared hydroxyhydroquinolphthalein (dihydroxyfluorescein) from hydroxyhydroquinol and phthalic anhydride. The constitution of hydroxyhydroquinolphthalein was investigated by Feuerstein and Dutoit.[4] Hydroxyhydroquinolbenzein, the mother substance, was prepared and studied by Liebermann and Lindenbaum[5] in 1904 and by Ghosh and Watson[6] in 1913. Osorovitz[7] condensed hydroxyhydroquinol with tetrachlorophthalic anhydride and obtained hydroxyhydroquinoltetrachlorophthalein.

The reaction between hydroxyhydroquinol and o-sulfobenzoic anhydride is analogous to that of the phenols as a class with phthalic anhydride to form various phthaleins.



Analysis of the hydroxyhydroquinolsulfonephthalein shows that its composition corresponds to that of the pyrone ring structure and the fact that its alkaline solution is quite fluorescent indicates that it is 2,7-dihydroxysulfonefluorescein (I).

Like other sulfonephthaleins which have been studied, it is tautomeric and gives colored derivatives of the quinoid form and colorless derivatives of the lactoid form. Since the sulfonephthalein itself is highly colored, it has been assigned the quinoid formula and is presumably an inner carbonium or oxonium salt. The crystalline product contains about

---

[1] From a dissertation presented by Mary L. Willard to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Liebermann, *Ber.*, 34,2299 (1901).

[3] Thiele and Jaeger, *ibid.*, 34,2617 (1901).

[4] Feuerstein and Dutoit, *ibid.*, 34,2637 (1901).

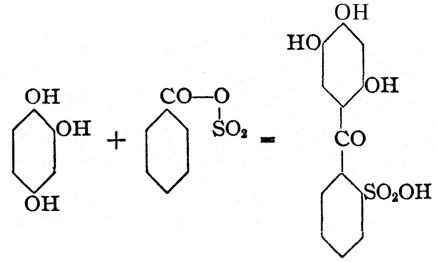
[5] Liebermann and Lindenbaum, *ibid.*, 37,1171 (1904).

[6] Ghosh and Watson, *Proc. Chem. Soc.*, **29,** 9 (1913).

[7] Osorovitz, *Ber.*, 36,1076 (1903).

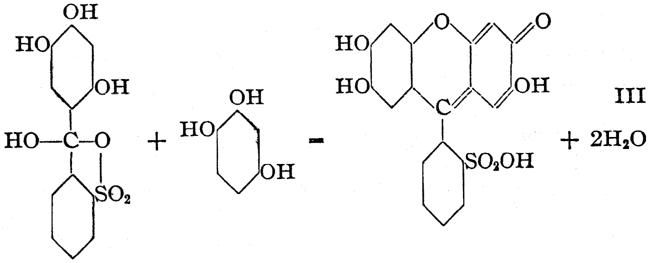
one-half a molecule of water per molecule of substance and is probably a solid solution of the quinoid, inner oxonium or carbonium salt, and the quinoid hydrate.

The formation of hydroxyhydroquinolsulfonephthalein takes place through an intermediate step, in' a manner similar to that observed with other sulfonephthaleins which have been prepared in this Laboratory. A tautomeric substance, 2',4',5'-trihydroxybenzoylbenzene-*o*-sulfonic acid, which is called the intermediate acid, is obtained by the action of one molecule of o-sulfobenzoic anhydride upon one molecule of hydroxyhydroquinol.



II

The second step in the formation of hydroxyhydroquinolsulfonephthalein is the condensation of 2',4',5'-trihydroxybenzoylbenzene-2-sulfonic acid (11) with a second molecule of hydroxyhydroquinol with the elimination of water (III).



III

That the intermediate acid is a tautomeric, y-ketonic acid is proved by preparing derivatives of both the ketone and lactone forms.

Hydroxyhydroquinolsulfonephthalein forms colored ethers, to which are assigned the quinoid structure.

Dibromohydroxyhydroquinolsulfonephthaleinwas isolated as a colored derivative which is also tautomeric. Since this dibromo derivative and its ammonium salt are colored, they are assigned the quinoid structure, while its tetra-acetate, which is colorless, is formulated as a derivative of the lactoid structure.

Concentrated sulfuric acid removes one molecule of water from the hydroxyhydroquinolsulfonephthalein, forming a violet-colored compound with a green luster, which has been given the name sulfoneviolein.

Hydroxyhydroquinolsulfonephthalein can be reduced with zinc dust, in formic acid solution, to hydroxyhydroquinolsulfonephthalin. The tetra-acetate of hydroxyhydroquinolsulfonephthalin and its silver salt have been prepared.

Experimental Part

In all calculations, 1925 atomic weights[8] were used. Carbon and hydrogen were determined by the usual combustion method with modifications of de Rhode for the presence of sulfur. Sulfur analyses were made in some cases with the Parr bomb, while in others Liebig's method of fusion with sulfur-free potassium nitrate and potassium hydroxide was used. Methoxyl and ethoxyl groups were determined by a modification of the Zeisel method.[9] Dennis' modification[10] of the Thiele apparatus was used to determine the melting points, which were uncorrected. A Bureau of Standards thermometer was used which was calibrated in 0.2°. In drying a substance to constant weight, an electrically heated tube[11] was used, through which was passed a slow current of dry air or carbon dioxide. The substance was introduced into this tube in a platinum boat on an asbestos support to prevent overheating by direct contact with the glass. The solubility of all salts was determined and classified according to Mulliken.[12]

All crystallographic data recorded were supplied by Professor Gill of the Department of Geology.

Preparation of Hydroxyhydroquinol.—Hydroxyhydroquinol was prepared from hydroquinol by oxidation to *p*-benzoquinone[13] with sodium dichromate in sulfuric acid solution and conversion of the latter into hydroxyhydroquinol tri-acetate according to a modification[14] of Thiele's method.[15]

The hydroxyhydroquinol tri-acetate was then hydrolyzed to hydroxyhydroquinol in the presence of hydrochloric acid.

2′,4′,5′-Trihydroxybenzoylbenzene-2-sulfonic Acid.—One hundred g. of hydroxyhydroquinol and **36** g. of o-sulfobenzoic anhydride[16] were heated at **100°** for eight hours. The orange-red mass was powdered and treated with distilled water. It was filtered

---

[8] G. P. Baxter, THIS JOURNAL, **47**, 600 (1925).

[9] Hewitt and Moore, *J. Chem. Soc.*, 81, **318 (1902)**; Hewitt and Jones, *ibid.*, 115, **193 (1919)**.

[10] Dennis, J. Ind. Eng. *Chem.*, 12, 366 **(1920)**.

[11] Chamot and Pratt, THIS JOURNAL, 32, **635 (1910)**; Orndorff and Nichols, ***Am. Chem.* J.**, 48, 477 **(1912)**.

[12] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1908, Vol. I, p. 38.

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. **85**.

[14] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1924, Vol. IV, p. **35**.

[15] Thiele, *Ber.*, 31, **1248 (1898)**.

[16] Cobb, **Am.** *Chem.* **J.**, 35, **502 (1906)**; White and Acree, THIS JOURNAL, 41, **1197 (1919)**. The saccharin used in this work was furnished gratis by the Monsanto Chemical Works, St. Louis, Mo.

to remove the insoluble material, hydroxyhydroquinolsulfonephthalein. The filtrate was repeatedly boiled with bone black and filtered until the solution became colorless. The solution was carefully concentrated to about **100** cc. and **50** cc. of concentrated hydrochloric acid was added. The intermediate acid separated in small colorless crystals.

Anal. Calcd. for $C_{13}H_{10}O_7S·2H_2O$: H_2O, **10.40.** Found: H_2O, **10.52, 10.44.** Calcd. for $C_{13}H_{10}O_7S$: mol. wt., **346.47;** S, **10.34;** C, **50.30; H, 3.25.** Found: (methyl red) mol. wt., **345.5, 346.9;** (phenolphthalein) mol. wt., **346.2, 346.8;** S, **10.10, 10.45;** C, **50.49, 50.81;** H, **3.29, 3.24.**

"Crystals of tabular, to thin, platey habitus reach a length of more than 2 mm. but are not perfect enough for gonimetric measurement. They are rhomboidal in shape, when well formed, and are certainly triclinic since extinction is not symmetrical and the bisectrix seen in converging polarized light is not normal to the surface of the plates. Double refraction is rather high and dispersion is strong."

The intermediate acid could also be separated from the fusion filtrate by precipitation of the barium salt with barium carbonate and subsequent acidification. The intermediate acid is very soluble in water; soluble in methanol, ethanol, acetone, ether and glacial acetic acid. It is difficultly soluble in benzene, xylene, petroleum ether and chloroform. The structure of the intermediate acid was proved by the method of Orndorff and Cornwell,[17] by fusion with potassium hydroxide at 210° for two hours. From the fused mass, after crystallization from 50% alcohol, small needles melting at 210° were obtained. This substance corresponded in properties to hydroxyhydroquinolcarboxylic acid (2′,4′,5′-trihydroxybenzoic acid).[18]

When 2′,4′,5′-trihydroxybenzoylbenzene-2-sulfonic acid was heated for three hours at 140°, it decomposed, forming hydroxyhydroquinolsulfonephthalein and o-sulfobenzoic anhydride. The intermediate acid reacted under similar conditions with hydroxyhydroquinol to form hydroxyhydroquinolsulfonephthalein. Several derivatives of the tautomeric forms of the intermediate acid **(2′,4′,5′-trihydroxybenzoylbenzene-2-sulfonic acid)** were made.

Ammonium Salt.[19]—Twenty-two *g.* of the acid ammonium salt of o-sulfobenzoic acid was heated with **12** *g.* of hydroxyhydroquinol at 190–195° for five hours. The fused mass was dissolved in hot water and recrystallized three times from hot water. The ammonium salt is very soluble in water, methanol or ethanol. It is insoluble in benzene, ether or petroleum ether.

Barium Salt.—Ten g. of the pure intermediate acid was boiled with **30** *g.* of barium carbonate for one hour. After the solution had been filtered, the barium salt of the intermediate acid crystallized from the concentrated filtrate. It was recrystallized

---

[17] Orndorff and Cornwell, THIS JOURNAL, 48, **986 (1926).**

[18] Thiele and Jaeger, Ber., 34, 2840 **(1901).**

[19] Analyses of the following compounds can be found in the thesis in the Library, Cornell University, Ithaca, New York.

twice from hot water. The barium salt is easily soluble in water, methanol and ethanol but very difficultly soluble in other organic solvents.

Zinc Salt.—Five g. of the pure intermediate acid was boiled with *25 g.* of zinc carbonate for one hour. The excess of zinc carbonate was removed by filtration and the filtrate was concentrated almost to dryness, when plate-like crystals separated which were recrystallized once from water. The colorless zinc salt crystallized with 5 molecules of water of crystallization. The zinc salt is soluble in water, methanol and ethanol but difficultly soluble in other organic solvents.

Tetra-sodium Salt.—Five g. of the pure intermediate acid was treated with the calculated amount of 0.1 N sodium hydroxide. The solution was evaporated to dryness and the salt recrystallized from water. The sodium salt is very soluble in water, methanol and ethanol. It is insoluble in ether, benzene and xylene.

Tetra-acetate.—Ten g. of pure dry intermediate acid was boiled with 100 cc. of acetic anhydride for three hours. The solution was filtered and about 50 cc. of acetic anhydride was distilled from the filtrate. Upon standing for twelve hours the colorless crystals separated from the solution. These were recrystallized twice from anhydrous ether. The tetra-acetate is soluble in ether and acetone but insoluble in benzene and petroleum ether. It is slowly hydrolyzed by long heating with water or alcohol.

Preparation of Hydroxyhydroquinolsulfonephthalein

(1) From the Anhydride of o-Sulfobenzoic Acid and Hydroxyhydroquinol Triacetate.—Hydroxyhydroquinolsulfonephthalein was prepared in the best yields by heating 200 g. of hydroxyhydroquinol tri-acetate with 70 g. of o-sulfobenzoic anhydride for eight hours at 140°. The last traces of acetic acid were removed by the use of reduced pressure. The mass, consisting of tiny green crystals, was purified by dissolving it in hot dilute sodium hydroxide and acidifying with dilute hydrochloric acid. The yield was 80%.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, **2.20.** Found: **2.16, 2.28.** Calcd. for $C_{19}H_{12}O_8S$: S, **8.01.** Found: S, **7.94, 7.97.**

(2) From the Chlorides of o-Sulfobenzoic Acid and Hydroxyhydroquinol.—Twenty-four g. of *o*-sulfobenzoic acid chloride and 28 g. of hydroxyhydroquinol were heated for three hours on a steam-bath and three hours more at 120°, using reduced pressure during the last hour. The product was purified as before. The yield was 40%. A small amount of material was insoluble in sodium hydroxide which was probably, if analogous to other sulfonephthaleins, the ester of o-sulfobenzoic acid.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, **2.20.** Found: **2.12, 2.16.** Calcd. for $C_{19}H_{12}O_8S$: C, **56.97;** H, **3.02;** S, **8.01.** Found: C, **56.97, 56.53;** H, **3.10, 3.09;** S, **8.03,** 7.86.

(3) From the Anhydride of o-Sulfobenzoic Acid and Hydroxyhydroquinol.—Eighteen g. of o-sulfobenzoic anhydride and 28 g. of hydroxyhydroquinol were heated at 130" for thirty hours. The product was purified as before. If a temperature higher than 130" was used, tar was formed; if lower, the yield rapidly decreased. The yield was 30%.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, **2.20.** Found: **2.17, 2.08.** Calcd. for $C_{19}H_{12}O_8S$: S, **8.01.** Found: **S, 7.46, 7.52.**

When anhydrous zinc chloride was used as a condensation agent, the yield was reduced to 15%.

Properties and Crystalline Form.—Professor Gill examined crystals of hydroxyhydroquinolsulfonephthalein prepared by fusion of the chlorides of o-sulfobenzoic acid and hydroxyhydroquinol. He stated: "The crystalline aggregates show bright yellow-green surface color, but do not have sufficiently sharp crystal boundaries to permit determination of the crystal system. They are nearly opaque except in very fine powder, when they appear to transmit a little reddish-brown colored light."

The green crystals of hydroxyhydroquinolsulfonephthalein, when ground in an agate mortar, formed a reddish-orange powder. Hydroxyhydroquinolsulfonephthalein is difficultly soluble in water, forming a red solution with green fluorescence. It is soluble in dilute (2%) sodium hydroxide, forming a red solution with green fluorescence. With concentrated (30%) sodium hydroxide, a fuchsin-colored solution is obtained. Concentrated sulfuric acid forms a yellow solution which is not fluorescent. Hydroxyhydroquinolsulfonephthalein is soluble in methanol, ethanol, acetic acid and acetone. It is insoluble in benzene, toluene, ether and petroleum ether. It can be precipitated from cold dilute alkaline solutions with dilute acid as a reddish powder and from hot solutions as fine green crystals. The PH was determined by Clark's colorimetric method[20] using a color chart found in Mulliken.[21] There was a change from OY to R at 7.2 and from VR to RV at 12.0.

The following derivatives of the tautomeric forms of hydroxyhydroquinolsulfonephthalein were made.

Ammonium Salt.--Samples of pure dry hydroxyhydroquinolsulfonephthalein absorbed 4 molecules of ammonia gas, a bluish-brown powder resulting, the aqueous solutions of which were fuchsin colored. When the tetra-ammonium salt was allowed to stand in an evacuated desiccator over sulfuric acid, a red stable mono-ammonium salt resulted. Hydrogen chloride gas did not form a stable compound with hydroxyhydroquinolsulfonephthalein.

Barium Salt.—Five g. of hydroxyhydroquinolsulfonephthalein and 30 g. of barium carbonate were boiled with 3 liters of water until all the sulfonephthalein had dissolved. After filtration and concentration of the filtrate, red crystals separated. The barium salt is very soluble in water, methanol and ethanol. It can be hydrolyzed with concentrated hydrochloric acid to the sulfonephthalein.

Zinc Salt.—An aqueous suspension of pure hydroxyhydroquinolsulfonephthalein was boiled with zinc dust until the solution became bright orange in color. After filtration, concentration and recrystallization from water, orange-red crystals were obtained. The zinc salt is soluble in water, methanol, ethanol and butanol.

Potassium Salt.—A sample of pure hydroxyhydroquinolsulfonephthalein was dissolved in the calculated amount of potassium hydroxide solution. The solution was filtered and the filtrate was concentrated. Reddish crystals separated. The potassium salt is readily soluble in most organic solvents.

Tetra-acetate.—A sample of pure dry hydroxyhydroquinolsulfonephthalein was heated for one hour with excess acetic anhydride. After solution had taken place,

---

[20] Clark, "The Determination of H-Ion Concentration," Williams and Wilkins Company, Baltimore, Maryland, 1922.

[21] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1908, Vol. 1.

about one-half the solvent was distilled off. Brownish-yellow needles separated from the remaining solution upon cooling. After three recrystallizations from acetic anhydride, colorless needles were obtained. The tetra-acetate was slowly hydrolyzed with water and more rapidly hydrolyzed with alkalies.

Tetra-benzoate.—A sample of pure dry hydroxyhydroquinolsulfonephthalein was boiled with excess benzoyl chloride for five hours. It was filtered and the filtrate was evaporated to dryness; the residue was extracted with hot benzene. The benzene extracts were concentrated in the presence of a little bone black. From the filtered suspension, small crystals separated upon cooling. They were twice recrystallized from benzene. The colorless tetra-benzoate is soluble in methanol, ethanol, ether, toluene, benzene and xylene. It is readily saponified with dilute sodium hydroxide and also boiling ethanol.

Sodium Salt of Trimethyl Ether.—Twenty g. of pure dry hydroxyhydroquinolsulfonephthalein was treated with methyl iodide and sodium methylate according to Claissen's method as used by Orndorff and Fuchs[22] in the preparation of pyrogallolsulfonephthalein and sulfonegallein ethers. About **20** g. of a dry green powder was obtained from the ether. The green powder was extracted with acetone. The acetone extracts were assembled and concentrated and a few red crystals were obtained which were recrystallized from acetone.

Anal. Calcd. for $C_{19}H_8O_5SNa(OCH_3)_3$: Na, **4.95; CH_3O, 20.05.** Found: Na, **5.07, 5.07; CH_3O, 20.05, 20.17.**

The sodium salt is easily soluble in most organic solvents. It does not form a blue solution with sodium hydroxide since the hydroxyl positions are already occupied and do not permit the formation of poly salts.

Trimethyl Ether.—The material left undissolved after the acetone extractions was dissolved in water and reprecipitated with hydrochloric acid. It was dried and extracted with boiling glacial acetic acid. The extractions were concentrated and a few reddish crystals were obtained which were recrystallized from methanol.

Anal. Calcd. for $C_{22}H_{18}O_8S$: S, **7.25.** Found: S, **7.40,** 7.50.

The trimethyl ether of hydroxyhydroquinolsulfonephthalein is soluble in most solvents except benzene and ether.

Dimethyl Ether.—The reddish material left undissolved after the extraction with boiling acetic acid was recrystallized four times from methanol.

Anal. Calcd. for $C_{19}H_{10}OS(OCH_3)_3$: **CH_3O, 14.49.** Found: **CH_3O, 14.39, 14.28.**

The dimethyl ether is soluble in water, methanol and ethanol. It is insoluble in ether, acetic acid, benzene and toluene.

Aniline Salt,—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in **200** cc. of aniline on a steam-bath. The solution was then heated for twelve hours at 120°. When the solution was cooled red needles separated. The crystals were filtered off and washed with ether. They did not melt below **300".**

"The dark reddish spongy masses appear to be made up of very small crystals, not more than 0.002 or 0.003 mm. in diameter. Nothing could be determined further than that the sparkling reflection from the surface indicated crystalline character."

Anal. Calcd. for $C_{19}H_{12}O_8S(C_6H_5NH_2)$: S, 6.50. Found: S, **6.38, 6.46.**

The red aniline salt is soluble in hot water and methanol. Aniline was liberated when the salt was treated with sodium hydroxide.

---

[22] Orndorff and Fuchs, THIS JOURNAL, **48,1939 (1926).**

Dibromohydroxyhydroquinolsulfonephthalein.—No reaction was observed between bromine and hydroxyhydroquinolsulfonephthalein in glacial acetic acid solution. Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 300 cc. of absolute ethanol and 20 g. of bromine in 100 cc. of absolute ethanol added. The solution was heated on a steam-bath for eight hours. When it had cooled green crystals separated which were purified by dissolving in water and precipitating with hydrochloric acid.

Anal. Calcd. for $C_{19}H_{10}O_8Br_2S\,2^1/_2H_2O$: H_2O, 7.48. Found: H_2O, 7.48, 6.90. Calcd. for $C_{19}H_{10}O_8Br_2S$: S, 5.75; Br, 28.65. Found: S, 5.82, 5.92; Br, 28.46, 28.20.

The dibromo derivative was soluble in water. It dissolved in dilute sodium hydroxide forming a red solution or a blue solution with more concentrated alkali. A color change was noted at P_H 6.4 from RO to VR.

Action of Ammonia.—Several samples of pure dry dibromohydroxyhydroquinolsulfonephthalein, when exposed to a stream of dry ammonia, absorbed 5.5 molecules of ammonia. After standing over sulfuric acid for some time a stable tri-ammonium salt resulted.

Tetra-acetate.—Ten g. of pure dry dibromohydroxyhydroquinolsulfonephthalein was boiled with 100 cc. of acetic anhydride for one hour. The solution was filtered into ice water. A brownish solid separated upon standing, which was purified by repeated recrystallization from benzene using bone black. This salt is very easily hydrolyzed with alkalies or water. It is soluble in benzene.

Sulfoneviolein.—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 10 cc. of concentrated sulfuric acid. The solution was heated for twelve hours at 120°. It was cooled and poured into ice water; a brownish-blue solid separated. It acquired a green luster upon drying and was recrystallized from nitrobenzene as fine green crystals.

Anal. Calcd. for $C_{19}H_{10}O_7S$: S, 8.39. Found: S, 8.46, 8.45.

It was insoluble in most organic solvents. It was slightly soluble in ethanol to a brown solution. It was soluble in acids to a red solution but was insoluble in alkalies.

Hydroxyhydroquinolsulfonephthalein.—Five g. of hydroxyhydroquinolsulfonephthalein was dissolved in about 200 cc. of formic acid. The solution was boiled with 10 g. of zinc dust. After about fifteen minutes it was completely decolorized. It was filtered in the presence of carbon dioxide. Upon cooling minute colorless crystals separated which were recrystallized from 50% formic acid.

Anal. Calcd. for $C_{19}H_{14}O_8S$: S, 7.97. Found: S, 8.22, 8.03.

"This substance is ocher yellow in mass, and a few of the larger crystals show pleochroism from buff to colorless. It is composed of sharply defined crystals, mostly 0.01 to 0.03 mm. in diameter. These have rather low double refraction and oblique extinction. The shape would seem to be monoclinic, though they may be triclinic."

The reduction product is soluble in most organic solvents. It oxidizes readily and becomes red upon standing in the air.

Tetra-acetate.—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 200 cc. of glacial acetic acid. Five g. of zinc dust and a few drops of copper sulfate (10%) solution were added. The mixture was boiled on a sand-bath for three hours. The acetic acid solution was filtered, concentrated to half the original volume and poured into ice water. A nearly colorless precipitate separated which was crystallized from 95% ethanol. The tetra-acetate of the reduction product was difficultly soluble in methanol, ethanol, benzene and acetone.

Anal. Calcd. for $C_{27}H_{22}O_{12}S$: S, 5.61. Found: S, 5.66.

Silver Salt of Tetra-acetate.—Five g. of hydroxyhydroquinolsulfonephthalein tetra-acetate dissolved in 200 cc. of absolute ethanol was added to 25 g. of silver nitrate dissolved in this alcohol, which had been previously boiled with other silver nitrate for one hour. After a few minutes' standing, fine colorless crystals separated. They were filtered off and allowed to dry in the absence of light. The silver salt was soluble in methanol and benzene but insoluble in most organic solvents.

Summary

1. 2′,4′,5′-Trihydroxybenzoylbenzene-2-sulfonic acid has been prepared. It has been shown that it is the intermediate step in the preparation of hydroxyhydroquinolsulfonephthalein. This intermediate acid is a γ-ketonic acid and acts as a tautomeric substance, giving derivatives of the ketone form and of the lactone form.

2. The preparation and properties of pure hydroxyhydroquinolsulfonephthalein have been studied. The best results were obtained by the condensation of hydroxyhydroquinol tri-acetate and o-sulfobenzoic anhydride. The product is dihydroxysulfonefluorescein formed by elimination of a molecule of water, with the production of a pyrone ring. Dilute alkaline solutions are fluorescent.

3. Since hydroxyhydroquinolsulfonephthalein is a highly-colored substance, it is represented as having the quinoid structure. It is tautomeric and yields colorless derivatives of the lactoid modification, as the tetra-acetate and tetra-benzoate, and colored derivatives of the quinoid structure, as the barium, zinc or potassium salts.

4. Colored di- and trimethyl ethers of hydroxyhydroquinolsulfonephthalein have been prepared, both of which are assigned the quinoid structure.

5. Dibromohydroxyhydroquinolsulfonephthalein and its ammonium salt were obtained as colored substances, to which the quinoid structure is assigned. The colorless tetra-acetate is considered to be a derivative of the lactoid structure.

6. Sulfuric acid removes a molecule of water from hydroxyhydroquinolsulfonephthalein, forming sulfoneviolein.

7. Hydroxyhydroquinolsulfonephthalin, the reduction product of hydroxyhydroquinolsulfonephthalein, its tetra-acetate and the silver salt of the tetra-acetate have been prepared. They are colorless and are easily oxidized.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, CHEMICAL AND TECHNOLOGICAL RESEARCH, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

STUDIES ON GOSSYPOL. V. THE ACTION OF CHROMIC ACID UPON SOME GOSSYPOL DERIVATIVES

BY E. P. CLARK[1]

RECEIVED NOVEMBER 3, 1928 PUBLISHED MAY 6, 1929

In a former paper[2] experiments were reported in which attempts were made to oxidize gossypol. The experience gained in this work indicated that, before this approach to the structural nature of the substance could be successful, the hydroxyl groups in the molecules would have to be protected.

Several derivatives fulfilling this requirement have been prepared, and their behavior toward various oxidizing reagents has been studied. This report is concerned with the products obtained by the action of chromic acid upon hexa-acetylgossypol, hexa-acetylapogossypol and apogossypol hexamethyl ether.

When dissolved in acetic acid and oxidized with an aqueous solution of chromic acid, hexa-acetylgossypol yields a bright yellow neutral compound which begins to darken at 210° and becomes a black mass at 230" without definitely melting. This substance has the molecular formula $C_{33}H_{30}O_{12}$. It possesses no carboxyl or free hydroxyl groups but has four acetyl groups and is, therefore, a tetra-acetyl derivative of a substance, $C_{25}H_{22}O_8$, to which the name *gossypolone* has been given. The derivative obtained is, therefore, tetra-acetylgossypolone. From a consideration of the foregoing it follows that in the formation of tetra-acetylgossypolone from hexa-acetylgossypol two acetyl groups are replaced by two quinone groups, and carbon and hydrogen are lost in such proportions that gossypolone has a lower molecular weight than gossypol by C_5H_8.

Tetra-acetylgossypolone readily condenses with aniline in much the same manner as does gossypol. The condensation product is a chocolate-colored micro-crystalline substance which imparts a deep wine-red color to solvents capable of dissolving it. It would appear from this that the two carbonyl groups originally in gossypol have not been affected by the oxidation.

When hexa-acetylapogossypol is treated in the same manner as hexa-acetylgossypol, except that Kiliani's chromic acid mixture[3] is used, a substance similar in appearance to tetra-acetylgossypolone is obtained. This is a neutral material having a melting point of 230° and a molecular formula

---

[1] This work was done under a research fellowship supported by the Interstate Cottonseed Crushers' Association.

[2] Clark, *J. Biol. Chem.*, **77, 81 (1928).**

[3] Kiliani, **Ber., 46, 676** (1913).

of $C_{30}H_{28}O_{10}$. It has been shown to be a tetra-acetyl derivative of a compound $C_{22}H_{20}O_6$. The name assigned to this substance is *apogossypolone*. In the reaction by which this material is formed, as in the previous one, two quinone groups have been substituted for two acetyl groups and the new non-acetylated derivative has a lower molecular weight than apogossypol by C_6H_{10}. One property of this new acetyl derivative which distinguishes it from tetra-acetylgossypolone is its inability to condense with aniline.

The oxidation of apogossypol hexamethyl ether with chromic and sulfuric acids (Kiliani's mixture) gave a bright yellow neutral crystalline compound, $C_{32}H_{34}O_8$, having a melting point of 210°. It has been established that this material is a tetramethyl ether of a tetraquinone, $C_{28}H_{26}O_8$. The name *pseudogossypolone* has been assigned this substance, and hence the C_{32} compound isolated is tetramethoxy-pseudogossypolone. The process by which it is formed is analogous to the reactions involving the acetyl derivatives discussed before, in that two quinone groups have been substituted for two methoxyl groups. On the other hand, methoxy derivatives of gossypol in general are far more resistant to reagents than the corresponding acetyl derivatives. In this experiment chromic acid did not attack the apogossypol molecule in such a manner as to cause a loss of carbon. Two quinone groups, however, were substituted for two hydrogen atoms.

The observations recorded concerning these new substances cannot be interpreted at present, since the loss of the elements, C_5H_8 and C_6H_{10}, without the introduction of oxygen into the molecule is a condition which could be explained by several possible types of reaction. Furthermore, the substitution of quinone groups for hydrogen atoms, or acetyl or methoxyl groups, as the case may be, points at present to the existence in the molecule of only aromatic nuclei. This conclusion, of course, has already been arrived at from previous work.

Some interesting observations relative to Zeisel determinations were made upon several gossypol derivatives. In the estimation of the methoxyl content of tetramethoxy-pseudogossypolone and of certain related compounds to be reported upon at a future time, difficulties arose which at first seemed to render the determinations impossible. Later, results were obtained, but they failed to harmonize with other information available. Finally, however, successful determinations were made but the rather unusual and anomalous data leading thereto were such that it was deemed desirable to record them separately in the report which follows.

Experimental

Tetra-acetylgossypolone.—Two grams of hexa-acetylgossypol dissolved in 50 cc. of boiling acetic acid was treated with 10 cc. of a 10% aqueous solution of chromium trioxide. The mixture was kept boiling for one minute after the addition of the reagent and then the oxidation was stopped by the addition of about 100 g. of crushed ice. The dilution caused the reaction product to separate as a bright yellow amorphous precipitate. It was freed from the mother liquor, washed with water and dried. The yield was 1.6 g. When this material was digested with approximately 20 cc. of boiling methanol, it quickly dissolved, but almost immediately a crystalline fraction began to separate. After some time the crystals were removed from the mother liquor, washed with methanol and dried. The yield of this product was 0.6 g. Crude amorphous acetylgossypol obtained directly from acetylating gossypol in pyridine solution gave the same results as the crystalline material. In a series of experiments 28 g. of the crude acetyl derivative gave 23 g. of the amorphous oxidation product, which yielded 11 g. of crystalline substance.

This material was purified by dissolving one part of the substance in ten parts of acetic acid-and adding five volumes of ether to this solution. Crystallization began immediately and was completed in a short time.

Thus purified, the substance consists of long bright yellow rods and needles which begin to darken at 210° and become a black mass at 230° without melting. Its indices of refraction are $n_\alpha = 1.559$; $n_\gamma = 1.676$ both ±0.003. The elongation is negative and the extinction is essentially straight (the extinction angle is very small).[4] The analytical data relative to this and to the other compounds under consideration are presented in Table I.

TABLE I

ANALYSIS OF OXIDATION PRODUCTS

Substance	Formula	Mol. wt.[a] Calcd.	Mol. wt.[a] Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Acetyl[b] Calcd.	Acetyl[b] Found
Tetra-acetyl-	$C_{33}H_{30}O_{12}$	618.4	622	64.06	64.10	4.89	4.80	4 groups,	24.02
gossypolone					64.03		4.79	27.83	24.00[c]
Tetra-acetylapo-	$C_{30}H_{28}O_{10}$	548.4	555	65.67	65.49	5.15	5.18	4 groups,	29.03
gossypolone					65.76		5.18	31.38	
Tetramethoxy								Methoxyl	
pseudogossy-	$C_{32}H_{34}O_8$	546.4	569	70.31	70.49	6.27	6.26	4 groups,	23.77
polone					70.34		6.15	22.7	23.79

[a] Rast, *Ber.*, 55, 1051 (1922).

[b] Perkin's N-Acyl method, *J. Chem. Soc.*, 87, 107 (1905).

[c] Recrystallized a second time from benzene and ether.

Tetra-acetylgossypolone—Aniline Condensation Product, $C_{33}H_{30}O_{12} + 2\ C_6H_5NH_2 \longrightarrow C_{45}H_{40}N_2O_{10} + 2H_2O$.—Tetra-acetylgossypolone was suspended in methanol and an excess of aniline was added. The quinone dissolved with the formation of a deep wine-colored solution from which the condensation product soon began to crystallize. The process was completed after several hours. The material was purified by dissolving it in a large volume of boiling benzene, filtering the hot solution and allowing the substance to crystallize from the filtrate. Thus purified, it consisted of clusters of minute spindle-shaped chocolate-colored crystals which began to soften at 250° and melted at 255–256° (corr.).

---

[4] The optical data reported in this communication were determined by Mr. George L. Keenan of the Food, Drug and Insecticide Administration of the Department of Agriculture.

Anal. Calcd. for $C_{45}H_{40}N_2O_{10}$: N, 3.64. Found: N, 3.61, 3.57.

Tetra-acetylapogossypolone.—Two g. of hexa-acetylapogossypol was dissolved in 100 cc. of boiling acetic acid and treated with 15 cc. of Kiliani's solution,[5] the reagent being added from a pipet during the course of half a minute. The reaction, which was vigorous, was terminated by adding about 300 g. of crushed ice. The yellow amorphous product was then treated with methanol as outlined in the foregoing experiment. The yield of the crude crystalline product was 0.45 g. or 29%. The material was recrystallized from boiling methanol. Thus purified, it consists of oblique prisms suggesting the common crystalline forms of gypsum. It begins to sinter at 220° and melts completely at 230° (corrected); $n_\alpha = 1.530$; $n_\gamma = 1.645$ (both ±0.003). The extinction on the elongated forms is straight and the sign of elongation is positive.

Tetramethoxypseudogossypolone.—This compound was prepared by essentially the same process that was used for the two substances just described. Two g. of apogossypol hexamethyl ether was dissolved in 100 cc. of boiling acetic acid and treated with 20 cc. of Kiliani's mixture in such a manner as to prevent too energetic boiling. After two minutes the reaction was stopped by adding about 200 g. of crushed ice. The yellow precipitate, which weighed 1.5 g., was dissolved in 20 cc. of boiling methanol and allowed to crystallize. The yield of the crystalline quinone was 0.4 g. It was recrystallized from its solution in 10 parts of acetic acid by the addition of 5 parts of methanol. Thus obtained, it consists of long yellow needles melting at 210° (corr.). Its indices of refraction are $n_\alpha = 1.585$; $n_\gamma = 1.700$ (both ±0.003). The extinction is inclined and the birefringence is strong.

Summary

Upon oxidation with chromic acid, hexa-acetylgossypol is converted into tetra-acetylgossypolone. In the reaction two acetyl groups are replaced by two quinone groups and the new non-acetylated substance has a lower molecular weight than gossypol by C_5H_8.

Hexa-acetylapogossypol yields by treatment with Kiliani's chromic acid mixture a new quinone, tetra-acetylapogossypolone. In this reaction two quinone groups are substituted for two acetyl groups and the apogossypol molecule loses the elements C_6H_{10}.

When oxidized with chromic and sulfuric acids, apogossypol hexamethyl ether loses two methoxyl groups, which are replaced by two quinone groups. Two hydrogen atoms are also oxidized to quinone groups. The new substance, $C_{32}H_{34}O_8$, is, therefore, a tetramethoxy derivative of a tetraquinone, $C_{28}H_{26}O_8$.

WASHINGTON, D. C.

---

[5] Four hundred g. of water, 80 g. of sulfuric acid and 53 g. of chromium trioxide.

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, CHEMICAL AND TECHNOLOGICAL RESEARCH, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

STUDIES ON GOSSYPOL. VI. THE ACTION OF BOILING HYDRIODIC ACID AS USED IN THE ZEISEL METHOD UPON GOSSYPOL AND SOME OF ITS DERIVATIVES. A SEMI-MICRO ZEISEL METHOXYL METHOD

BY E. P. CLARK[1]

RECEIVED NOVEMBER 3, 1928 PUBLISHED MAY 6, 1929

In the preceding report[2] it was stated that difficulties arose in determining the methoxyl content of various methylated derivatives of gossypol, especially tetramethoxypseudogossypolone. When treated in the usual manner with hydriodic acid in a Zeisel apparatus, this substance gave practically no silver iodide. The addition of acetic acid or acetic anhydride to the hydriodic acid was also without appreciable effect. For example, in one experiment about 4% of methoxyl was obtained after the substance was boiled for four hours; whereas, if there are 4 methoxyl groups in the compound, as other evidence indicates, the theory demands a methoxyl content of 22.7%. In another experiment, phenol was added to the hydriodic acid, as recommended by Weishut.[3] When this was done, the white double compound of silver nitrate and silver iodide immediately formed. Since the first experiments indicated the advisability of running the determination for a longer time than is usually required, boiling was continued for three and one-half hours. When the final result was obtained, it was found rather unexpectedly that the methoxyl content corresponded to five groups more closely than to four.

In view of the combustion results and other information available, it seemed improbable that the compound had more than four methoxyl groups and, therefore, some other cause was responsible for the high value. Further investigation revealed that, when phenol was used with hydriodic acid in the Zeisel method, all gossypol derivatives tried, as well as gossypol itself, gave upon prolonged boiling a small quantity of silver iodide. When the silver iodide was calculated to methoxyl, an average of 81% of that required for one methoxyl group was obtained. This result was unusual since the oxygen in all the substances investigated was accounted for in forms other than alkoxyl groups. It was then demonstrated that the silver iodide was not derived from methyl iodide or from the reagent and, further, that the apparatus was not responsible for it.

These facts were proved by running blank determinations on the reagents

---

[1] This work was done under a research fellowship supported by the Interstate Cottonseed Crushers' Association.

[2] Clark, THIS JOURNAL, 51, 1475 (1929).

[3] Weishut, *Monatsh.*, 33, 1165 (1812).

and by using the method of Willstatter and Utzinger[4] in which the alkyl iodide was caught in trimethylamine and the solubility of the addition product was studied. In performing this experiment, hexa-acetylapogossypol was employed. From analysis it was known that this material gives silver iodide equivalent to 3.9% of methoxyl. With this in mind, a quantity of the acetyl derivative equivalent to 7 mg. of methoxyl was treated in the Zeisel apparatus as described under "Experimental," and the alkyl iodide was collected in trimethylamine solution. No insoluble addition product formed, however, although in a control experiment with a quantity of a known compound equivalent to **3** mg. of methoxyl, sufficient tetramethylammonium iodide was precipitated to make it possible to obtain 10 mg. of the material in a pure dry condition. These facts showed, although indirectly, that the alkyl iodide was not methyl iodide and hence was not derived from a methoxyl group. This does not in itself exclude the possibility of the presence of other alkoxyl groups, but their existence seems impossible since all of the oxygen in the gossypol derivative used in this experiment is accounted for as acetyl groups.

In view of these results, the most plausible explanation of this unusual situation is that prolonged heating of these compounds with the reagents used causes the gossypol nucleus to decompose in such a manner as to yield an alkyl iodide. One process by which this could be accounted for is the formation of formaldehyde which, with hydriodic acid, would yield methylene iodide, finally resulting in the production of silver iodide.

In this work it was not feasible to use the ordinary macro-Zeisel method on account of the lack of a plentiful supply of the material. Neither was a strictly micro-Pregl methoxyl determination possible because of not having the necessary equipment, especially a micro-balance. A method based largely upon Pregl's work, however, was adopted in which samples of about 20 mg. were successfully analyzed, employing an ordinary analytical balance sensitive to 0.1 mg. Since this procedure was developed for this investigation, the following description of the apparatus and the technique employed in the determination is given.

Incidentally, by this method the methoxyl content of apogossypol hexamethyl ether, previously reported[5] as entirely resistant to boiling hydriodic acid, has been determined.

Experimental

Determination of Methoxyl Groups on Samples of Approximately 20 **Mg.**—The apparatus employed for this purpose is shown with all necessary specifications in Fig. 1.

Approximately 20 mg. of substance upon a balanced piece of cigarette paper 2 by **3** cm. is weighed on an ordinary analytical balance sensitive to 0.1 mg. The paper containing the substance is placed in the bottom of the boiling flask, **A,** together with a

---

[4] Willstatter and Utzinger, ***Ann.,*** 382, 148 (1911).

[5] Clark, **J.** *Biol.* Chem., **78, 165** (1928).

boiling rod.[6] About 2.5 cc. of melted phenol and 5 cc. of constant boiling hydriodic acid solution of the quality employed in Zeisel determinations are added. The flask is connected by tension springs to the remainder of the apparatus, which consists of the trap B containing a small quantity of red phosphorus, suspended in water, and the receivers C, and D, containing alcoholic silver nitrate. The phosphorus is purified according to the directions of Pregl[7] and is used in the same manner except that one charge may be employed for four or five determinations. The alcoholic silver nitrate solution is also prepared according to Pregl. Seven cc. are used in C and 4 cc. in D. A slow, uniform stream of carbon dioxide is passed through the capillary side arm of the boiling flask and the liquid is gently boiled by means of a mantled microburner at such a rate that the vapors of the boiling liquid rise to approximately 8 cm. from the first bend in the air condenser. After about three minutes the white double compound of silver nitrate and silver iodide appears in the first silver nitrate tube. For most substances thirty minutes is sufficient to complete the reaction and sweep out the apparatus. The contents of both the tubes C and D and any precipitate adhering to the adapter are washed into a 150-cc. beaker with approximately 75 cc. of water. The liquid is made acid with nitric acid and allowed to stand on a steam-bath overnight, or until all of the silver iodide has separated and the mother liquors are entirely clear.

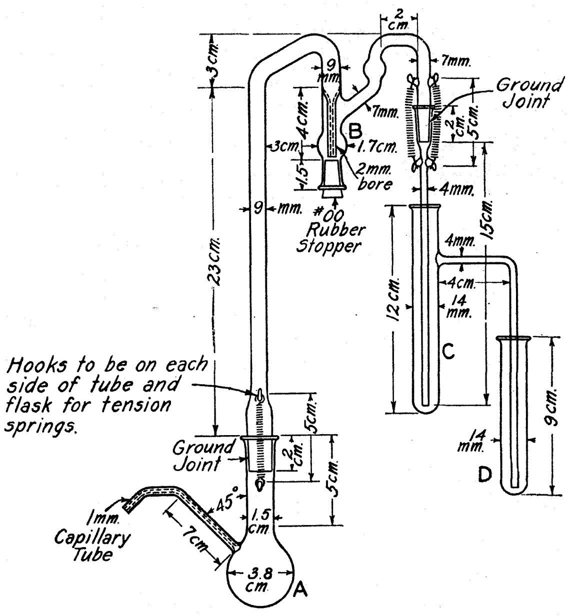


Fig. 1.—Semi-micro Zeisel methoxyl apparatus.

---

[6] The boiling rod used here is a glass tube approximately 60 mm. long, 3.5 mm. outside diameter, with a 1-mm. bore. It is sealed at one end and also closed about 10 mm. from the other. The open end is fire polished. When this is placed in the flask with the open end down, it will cause uniform boiling indefinitely so long as sufficient heat is constantly applied to the liquid.

[7] Pregl, "Quantitative Organic Microanalysis," Translated by Fyleman, P. Blakiston's Sons and Company, Philadelphia, 1924, p. 155–156.

The precipitate is transferred to a sintered-glass Pregl filtering tube having a porosity less than 7, in accordance with the technique of Pregl.[8] After the silver iodide is thoroughly washed, it is dried at 100° to constant weight. Usually half an hour is sufficient for this purpose. When the tubes are being weighed before and after collecting the silver iodide, another tube of the same type and size is always used as a tare.

The apparatus and procedure were tested on pure vanillin and α-methylglucoside. The results obtained are recorded in Table I.

TABLE I

RESULTS OBTAINED IN TESTING THE SEMI-MICRO ZEISEL METHOD

Substance	Sample, mg.		AgI, mg.		Methoxyl, % Calcd.	Methoxyl, % Found	
Vanillin	21.2	20.3	32.3	31.4	20.40	30.23	20.44
or-Methylglucoside	21.4	20.6	25.6	24.9	15.98	15.81	15.97

When these experiments were repeated without phenol, the results were uniformly about 0.5% low.

TABLE II

METHOXYL VALUES OF SOME GOSSYPOL DERIVATIVES AS INFLUENCED BY THE DURATION OF BOILING

Substance	Sample, mg.	AgI obtained, mg.	Period of boiling. hours	OCH_3 found. %
Tetramethoxypseudogossypolone; mol. wt.,	20.9	37.6	0.5	23.77
546.4; calcd. for 4 OCH_3 groups, 22.7%	20.5	36.9	0.5	23.79
of methoxyl	21.8	44.5	3	27.0
	21.8	44.7	3	27.1
	25.4	52.7	6	27.4
Apogossypol hexamethyl ether; mol. wt.,	21.1	54.8	0.5	34.32
546.5; calcd. for 6 OCH_3 groups, 34.07%	20.5	53.0	0.5	34.17
of methoxyl	20.4	58.4	4	37.83
	20.3	58.0	4	37.76

In Table III data are given showing the quantity of silver iodide obtained from several gossypol derivatives upon prolonged boiling (three to four hours). The oxygen in all of these substances is accounted for in forms other than alkoxyl groups.

TABLE III

SHOWING THE YIELD OF SILVER IODIDE OBTAINED FROM SOME GOSSYPOL DERIVATIVES

Substance	Mol. wt.	Sample, mg.	AgI obtained, mg.	Calcd. to methoxyl, %
Gossypol	518.4	21.4	9.2	5.7
Apogossypol hexa-acetate	714.5	20.2	5.9	3.9
Apogossypolone tetra-acetate	548.4	20.7	8.1	5.2
Hexa-acetylgossypol	770.5	21.6	3.3	2.0
Tetra-acetylgossylpolone	618.4	20.0	5.9	3.9

From the figures presented before concerning tetramethoxypseudogossypolone and apogossypol hexamethyl ether, it will be seen that in the former

---

[8] Ref. 5, p. 113.

instance three to six hours' boiling gave results from 4.4 to 4.7% high; whereas in the latter case the results were 3.7% high. These quantities, in excess of that demanded by theory, are of the same order of magnitude as those obtained on the products recorded in Table III.

Summary

In the Weishut–Zeisel methoxyl determination, gossypol and some of its derivatives, although containing no *alkoxyl* groups, yield upon prolonged boiling a small quantity of silver iodide.

The silver iodide thus formed is responsible in some cases for the abnormally high values obtained in the Zeisel determination of the methoxyl groups in several oxymethylgossypol derivatives.

The explanation has been advanced that under the conditions of the Weishut–Zeisel determination the gossypol nucleus is disrupted in such a manner as to yield an alkyl iodide. This iodide, however, is not methyl iodide.

A description is given of an apparatus and a procedure for the determination of methoxyl groups in samples of the order of 20 mg. In this method an ordinary analytical balance sensitive to 0.1 mg. is employed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE PREPARATION AND PROPERTIES OF THE ISOMERIC HEPTANES. PART I. PREPARATION[1]

BY GRAHAM EDGAR, GEORGE CALINGAERT AND R. E. MARKER

RECEIVED NOVEMBER 7, 1928 PUBLISHED MAY 6, 1929

I. Introduction

In connection with a study in this Laboratory of certain properties of aliphatic hydrocarbons, it was decided to investigate each of the nine isomeric heptanes. This group includes nearly every type of structure which an aliphatic hydrocarbon may have, and yet is not too large to make its synthesis impracticable.

Only one of the heptanes, the normal, was available in reasonable quantity, from Jeffrey pine oil.[2] The others were synthesized in considerable quantities by methods described below.

Inspection of the literature showed that the data on physical properties of even normal heptane leave much to be desired, although the work of Kremers and others in recent years has increased considerably our knowledge of this hydrocarbon. Few reliable data were available in the older

---

[1] Presented at the Symposium on Organic Chemistry, Columbus, Ohio, December 29. 1927.

[2] E. Kremers, J. Am. *Pharm. Assocn.*, 9, 857 (1920).

literature on the properties of any of the other isomers. Chavanne and his co-workers[3] have recently synthesized several of the isomers and determined some of their properties. The amounts synthesized, however, were small, and the authors scarcely attempted to determine the properties of the compounds beyond what was necessary for identification. It was therefore decided to measure with reasonable accuracy such physical properties of these hydrocarbons as could be conveniently measured in this Laboratory, and to enlist the aid of other laboratories well equipped to measure other properties. From these investigations there has resulted a rather complete collection of data concerning these heptanes. The data are of particular interest in that all of them were obtained on the same actual samples of material. Some of the data have been already published,[4] and other data will be published later.

Part I of this paper presents the methods of preparation of the heptanes and such physical properties as are commonly employed for purposes of identification. Part II will summarize the entire data, published and unpublished, referred to above, and will discuss the effect of structure upon physical properties in general, and upon certain physical properties in particular.

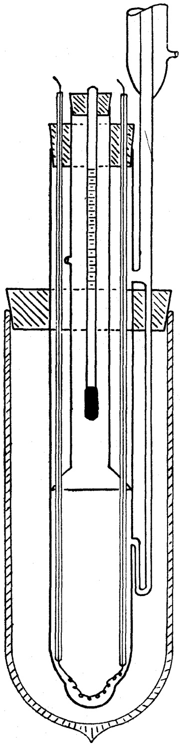


Fig. 1.

II. Experimental

(1) Methods of Synthesis.—Six of the nine heptanes were prepared by the method which has become classical since its systematic use by Chavanne and his co-workers.[3] It consists in the condensation by means of a Grignard reaction of two suitably chosen radicals, one being present as alkyl halide, the other as aldehyde, ketone or ester. The resulting secondary or tertiary alcohol is dehydrated, and the unsaturated hydrocarbon or hydrocarbons so formed, hydrogenated. This general method had to be modified slightly to fit each individual case. A complete description is given therefore in one case, only the variations being specified for the other preparations.

Of the three other heptanes, the normal is already available from Jeffrey pine oil.[2] The other two, 2,2-dimethylpentane and 3,3-dimethyl-

---

[3] (a) Chavanne and Simon, *Compt. rend.*, 168, 1324 (1919); (b) Chavanne and Lejeune, *Bull. soc. chim. belg.*, 31, 98 (1922); (c) Chavanne and DeGraef, *ibid.*, **33**, *366* (1924); (d) DeGraef, *ibid.*, 34, 427 (1925).

[4] C. P. Smyth and W. N. Stoops, THIS JOURNAL, 50, 1536 (1928); G. W. Stewart, *Phys. Rev.*, 32, 1153 (1928); Freyer, Hubbard and Andrews, THIS JOURNAL, **51**, 759 (1929); M. S. Kharasch, *Bureau of Standards Journal of Research*, 2, *373* (1929).

pentane could not be obtained pure by the general method of preparation (see Note 2, p. 1487) and their synthesis is fully described hereunder.

The main object of the work being the preparation of the heptanes in a state of high purity, comparatively little attention was paid to the intermediate products. The boiling points and specific gravities mentioned here for the alcohols and olefins are to be taken more as indications of the distillation cuts which were used than as accurate physical constants of these compounds. The boiling range given for the heptanes, however, represents the *entire boiling range* of the refractionated sample, temperatures being taken at the top of an efficient column. The alcohols obtained are always individual compounds, while the olefins may be mixtures of two or more isomers, differing only by the position of the double bond. The quantities given here refer to the size of a batch in each preparation, the total amount of heptanes prepared and purified being given at the end. The yields given are those obtained on the preparations as described. No doubt some of them at least could be improved by a careful study of the reaction.

The general method of preparation is fully described in the case of 2-methylhexane. The other preparations are given in tabular form.

2-Methylhexane

(a) 2-Methyl-2-hexanol.—To a solution of the Grignard reagent prepared from 6.5 moles of magnesium and 6.5 moles of n-butyl bromide in 2500 cc. of anhydrous ether was added slowly with stirring 6 moles of very pure acetone in an equal volume of anhydrous ether. After standing overnight, the mixture was decomposed by water and ice. More ice was added and the precipitated magnesium compounds dissolved in 10% hydrochloric acid. The ether layer was separated, washed with dilute sodium carbonate, with distilled water, then dried with anhydrous sodium sulfate and fractionated; yield. 640 g. (92%); b. p. 137–141°; d_{20}^{20}, 0.815.[5]

(b) 2-Methyl-2-hexene.—A mixture of 580 g. of the carbinol (a) and 1 g. of iodine was slowly distilled, keeping the distilling temperature at 81–83°. The distillate was washed with a sodium thiosulfate solution, with distilled water, then dried with calcium chloride and twice fractionated over metallic sodium; yield, 465 g. (95%); b. p. 94.5–96°.[6]

(c) **2-Methylhexane.**—By means of a nickel catalyst at 150°, 465 g. of the olefin (b) was hydrogenated. One passage over the catalyst gave nearly complete reduction, as shown by titrating a sample with bromate–bromide solution. The product was shaken with several portions of concd. sulfuric acid until a fresh lot of acid showed no yellow color. It was washed with water, then dried over calcium chloride, refluxed over sodium for several hours and then fractionated from sodium; yield 385 g. (82%); b. p. 89.7–90° (760 mm.).

---

[5] The density of the carbinols was determined roughly by means of a Westphal balance.

[6] It was found inadvisable to dehydrate the alcohol by means of *p*-toluenesulfonic acid because the introduction of sulfur compounds caused poisoning of the catalyst. The use of the sulfonic acid also gave a product of much wider boiling range, indicating the presence of isomeric olefins.

Preparation of the Carbinols

The following carbinols were prepared by the Grignard reaction as outlined above.

TABLE IA

REAGENTS

Halide	Moles	Carbonyl compound	Moles
n-Propyl bromide	4	Methylethyl ketone	4
Ethyl bromide	4	Ethyl propionate	2
Isobutyl bromide	4.5	Acetone	4
Sec.-butyl bromide	3	Acetone	3
Tert.-butyl chloride	4	Acetone[a]	3

[a] The acetone used must be of very high purity; otherwise polymerization occurs and no alcohol is obtained.

TABLE IB

PRODUCTS AND OTHER DATA

Product	Yield g.	Yield %	B. p., °C.	d_{20}^{20}
3-Methyl-3-hexanol	297	64	137–139	0.823
3-Ethyl-3-pentanol[a]	194	83	140–142	.839
2,4-Dimethyl-2-pentanol	252	54	127–129	..
2,3-Dimethyl-2-pentanol	122	35	129–130.5	.805
2,2,3-Trimethyl-3-butanol[b]	97	28	130	..

[a] This alcohol dehydrates very easily. If it is desired to isolate it pure, it is advisable to avoid entirely the presence of iodine.

[b] The carbinol melts at 17°. It is very hygroscopic and forms a hydrate with m. p. around 80°. When it is distilled in small amounts and without special precautions, only the hydrate is obtained. When larger quantities are handled, the distillate is a mixture of the liquid carbinol and of acicular crystals of its hydrate. The carbinol crystallizes instantly when shaken with a small amount of water. The hydrate loses its water readily when kept in a desiccator over barium oxide.

Preparation of the Olefins

The olefins were prepared from the corresponding carbinols as described above.

TABLE II

REAGENTS, PRODUCTS AND DATA

Carbinol used	G.	Product	Yield g.	Yield %	B. p., °C.
3-Methyl-3-hexanol	297	3-Methyl-3-hexene	234	93	93–96
3-Ethyl-3-pentanol	116	3-Ethyl-2-pentene	93	95	95–97
2,4-Dimethyl-2-pentanol	232	2,4-Dimethyl-2-pentene	178	91	81–83
2,3-Dimethyl-2-pentanol	588	2,3-Dimethyl-2-pentene	324	54	92–95
2,2,3-Trimethyl-3-butanol	348	2,2,3-Trimethyl-3-butene	279	95	76–78

Reparation of the Heptanes

The olefins were hydrogenated as described above.

TABLE III

REDUCTION OF OLEFINS

Olefin	G.	Product	Yield g.		B. p., °C. (760 mm.)
3-Methyl-3-hexene	234	dl-3-Methylhexane	206	87	91.4–91.7
3-Ethyl-3-pentene	292	3-Ethylpentane	238	80	93.2–93.5
2,4-Dimethyl-2-pentene	245	2,4-Dimethylpentane	202	81	80.5–81.1
2,3-Dimethyl-2-pentene	360	*dl*-2,3-Dimethylpentane	290	87	89.5–89.9
2,2,3-Trimethyl-3-butene[a]	284	2,2,3-Trimethylbutane	250	86	80.9–81.2

[a] The heptene hydrogenated very readily on one passage through the catalyst tube.

2,2-Dimethylpentane.—To the Grignard reagent prepared from 4 moles each of magnesium and n-propyl bromide were added with vigorous stirring 4 moles of *tert.*-butyl chloride and 30 g. of mercuric chloride. Some gas was evolved and the mixture soon settled to a compact solid. After standing overnight the mixture was decomposed as usual. The ether layer was washed, dried and fractionated. The fraction boiling above 50° was washed with cold concd. sulfuric acid several times, with sodium carbonate solution, then dried with calcium chloride, refluxed over sodium for several hours and finally fractionated from sodium; yield, 84 g. (21%); total hydrocarbon prepared, 240 g.; b. p. 78.2–79.5° (760 mm.).

3,3-Dimethylpentane.—This was prepared in a similar way by treating the Grignard reagent from 9 moles of ethyl bromide with 6 moles of *tert.*-amyl chloride and 30 g. of mercuric chloride; yield, 77 g. (13%); total hydrocarbon prepared, 77 g.; b. p. 85.7–86.1° (760 mm.).

NOTE 1.—The low yields obtained with the last two hydrocarbons are due to side reactions giving octane and hexane in one case, and decane and butane in the other, and also to the removal of halogen acid to form olefins in both cases. In a second preparation of 3,3-dimethylpentane a yield of 27% was obtained.

NOTE 2.--Several attempts were made to prepare these two hydrocarbons by the methods employed with the other hydrocarbons. These attempts were unsuccessful due to rearrangements which took place on dehydrating the alcohols.

(a) 2,2-Dimethyl-3-pentanol, from 5 moles of *tert.*-butyl chloride and 1.65 moles of propionaldehyde by the Grignard reaction; yield, 116 g. (60%); b. p. 136–137°; d_{20}^{20}, 0.826.

(b) Over 400 g. of this carbinol was dehydrated either with iodine, zinc chloride or *p*-toluenesulfonic acid. The corresponding bromide was also changed to the olefin by heating with quinoliie. In every case the resulting heptene showed a very wide boiling range (80–90°, mostly 88–90°). No heptane of satisfactory purity could be obtained from it. A study of the physical properties of the product showed it to be a mixture of 2,2-dimethyl- and 2,3-dimethylpentane.

(c) 3,3-Dimethyl-2-pentanol from 4 moles each of *tert.*-amyl chloride and acetaldehyde; yield, 144 g. (36%); b. p. 147–148°; d_{20}^{20}, 0.829.

(d) Dehydration and hydrogenation again gave a mixture of heptanes, 3,3-dimethyl- and 2,3-dimethylpentane, the latter predominating.

These experiments indicate that on dehydration 2,2-dimethyl-3-pentanol and 3,3-dimethyl-2-pentanol rearrange to a large extent, either by direct migration of a methyl group, or by intermediate formation of a cyclopropane ring. The latter course does not seem unlikely to be the one followed, in light of the rearrangements discussed by Brooks.[7]

Normal **Heptane.**—This is now available in large quantities from Jeffrey pine oil.[2]

---

[7] Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922, p. 70.

A product of this origin was purified from a small amount of terpene and aldehyde either by treatment with iodine[2] or by shaking with sulfuric acid and then with aqueous potassium permanganate. The final product, fractionated over sodium, showed a very sharp boiling point, indicating the absence of other hydrocarbons of the paraffin series. It may also be prepared by either one of the methods outlined above. Another method which has been used successfully by the authors is the reduction of n-heptyl bromide by sodium in liquid ammonia, according to the method described elsewhere for the preparation of *n*-butane.[8]

(2) Measurement of Boiling Point, Refractive Index, Specific Gravity, Freezing Point and Critical Temperature of Solution in Aniline

Boiling points were measured in an apparatus outlined in Fig. 1, employing internal electric heating, vapor lagging of the thermometer, protection from radiation losses by a vacuum flask and, of course, appropriate corrections for thermometer error and barometric pressure.

Refractive indices were measured in an Abbé refractometer, employing sodium light. Since the data were later determined with greater precision by Smyth,[4] his data, which agreed very well with those of the authors, have been employed. Specific gravities were determined in a 25-cc. Sprengel pycnometer at two temperatures near 20°. The data are practically identical with those determined later by Smyth and Stoops.[4]

Melting points were determined by Dr. R. N. Pease, of Princeton University, to whom the authors are much indebted for the actual measurements and for permission to include them in this paper. The method employed was the use of a three-junction copper–constantan thermocouple and a sensitive potentiometer carefully calibrated against the melting

TABLE IV

PHYSICAL PROPERTIES OF THE HEPTANES

	B. p. (760 mm.), °C.	M. p., °C.	d_4^{20} [a]	n_D^{20}	C.T.S. (aniline), °C.
n-Heptane	98.4	− 90.5	0.6836	1.38777	70.0
2-Methylhexane	90.0	−119.1	.6789	1.38509	74.1
3-Methylhexane	91.8	.....	.6870	1.38873	70.5
3-Ethylpentane	93.3	.....	.6984	1.39366	66.3
2,2-Dimethylpentane	78.9	−125.6	.6737	1.38233	77.7
2,3-Dimethylpentane	89.7	.....	.6952	1.39201	68.1
2,4-Dimethylpentane	80.8	−123.4	.6745[b]	1.38233	78.8
3,3-Dimethylpentane	86.0	−135.0[c]	.6934	1.39114	71.0
2,2,3-Trimethylbutane	80.9	− 25.0	.6900	1.38940	72.4

[a] The average temperature coefficient of specific gravity is 0.00085 per degree.

[b] A later preparation gave a material of d_4^{20}, 0.6731, indicating a possible error in the earlier determination. The difference, however, is, not sufficient to affect any of the conclusions drawn in Part II of this paper.

[c] This value was determined by Dr. George S. Parks, of Stanford University, to whom the authors are very much indebted.

---

[8] G. Calingaert and L. B. Hitchcock, THIS JOURNAL, 49, 750 (1927).

points of monochlorobenzene, toluene, carbon disulfide, ethyl ether and the sublimation point of carbon dioxide. Unfortunately four of the isomers could not be frozen, but solidified to a glass. Apparently the increasing viscosity and low melting points of some of the isomers make it very difficult to freeze them, as the same difficulty has been reported by Timmermans?[9] It is hoped that the melting points of all of the isomers may eventually be determined.

Critical solution temperatures in aniline are frequently employed for identification of hydrocarbons and were therefore determined for the isomers in an air-jacketed test-tube, using freshly distilled C. P. aniline and making appropriate thermometer correction.[10] These data are summarized in Table IV.

III. Discussion

(a) Synthetic Methods.—While there is nothing particularly novel about the methods employed in the synthesis of these hydrocarbons, the results obtained serve to illustrate the value of the carbinol–olefin–paraffin method. It is theoretically possible to prepare any paraffin by these methods; in most cases the raw materials are available, not too expensive and the reactions direct and clean cut. It is clear, however, from the discussion in Note 2 that care must be taken in interpreting the course of the reactions, particularly when dehydrations are involved of carbinols in which the alcohol group is adjacent to a tertiary group. Rearrangement is usually indicated by a wide boiling range in the dehydrated product, but may be so complete as to be unnoticed. In the present work identification of the compounds was aided by the fact that all of the possible isomers were prepared.

When the raw materials involved are sufficiently inexpensive the present modification of the Würtz synthesis (preparations of 2,2- and 3,3-dimethylpentane) is time saving and fully satisfactory from the standpoint of purity, although the yields are low.

The two preparations in which this synthesis was employed involved the reaction of tertiary halides, and it is not established that other halides will behave similarly. The chlorides of other heavy metals have been employed by the authors for similar syntheses, with varying degrees of success.

(b) Probable **Purity** of **the** Hydrocarbons.—In a group of hydrocarbons like the heptanes the determination of purity is somewhat difficult. Absence of extraneous substances may be easily assured and the presence of paraffins other than heptanes is usually unlikely; the freedom from isomers is more difficult to detect. There are no specific chemical tests and the ordinary physical properties such as boiling point, refractive index and

---

[9] Timmermans, *Bull. soc. chim. belg.*, 36, 502 (1927).

[10] These values were determined by Mr. D. T. Flood of this Laboratory.

density, are little separated in some cases. Freezing point measurements would show more variation but these are not available in all cases. For preparations in question the sharpness of boiling points of the purified products, combined with the available data on melting points and other properties, indicates that the compounds were unusually pure and free from other isomers. This makes the data on their physical properties particularly valuable.

(c) Comparison of the Physical Data with the Literature.—In general there is good agreement with the most reliable data in the literature, though a few exceptions deserve mention.

3-ETHYLPENTANE

Data of	Konovalow[11]	"Int. Crit. Tables"	Authors
B. p., °C.	95–98	93.8	93.3
d_4^{20}	0.695 (extrapolated)	0.670	0.6984

Konovalow's data agree with those of the authors sufficiently for a product which was admittedly not very pure. The boiling point given in "International Critical Tables" from an unknown source appears to be a little high, while the density is so low as to suggest a typographical error. The detailed discussion of the variation of physical properties with structure, which will be presented in Part II, will show that it is highly improbable that this isomer should have a density lower than that of normal heptane.

2,2-DIMETHYLPENTANE

Observer	DeGraef[3d]	Timmermans[8]	Authors
M. p., °C.		-137.0	-125.6

A private communication from Professor Timmermans has advised the authors that the above figure was in error on account of a faulty thermometer. Professor Timmermans has recalculated his own data and reports the corrected value as -122.5".

2,4-DIMETHYLPENTANE

Data of	Chavanne and DeGraef[3]	"Int. Crit. Tables"	Authors
B. p., °C.	80.9	83.9	80.8
d_4^{20}	0.6731	0.681	0.6731
M. p., °C.	-119.4	......	-123.4

Here again the figures given in "International Critical Tables" appear to the authors to be of doubtful value. Both the boiling point and density are almost certainly too high. The discrepancy of 4° between the melting point reported by Chavanne and that of the authors does not seem to be accounted for by impurities in the authors' sample because of the nature of the cooling curve obtained, which could not be interpreted so as to change the recorded value by more than one degree.

[11] Konovalow, *Chem.* Centr., I, 2143 (1908).

Summary

The nine isomeric heptanes have been obtained in considerable quantity and excellent purity and have been identified with certainty. One was isolated from a natural product and the other eight were prepared by two methods, alcohol–olefin–paraffin and modified Wiirtz. Their boiling points, specific gravities, refractive indices and critical solution temperatures in aniline are presented, with the melting points of five of them.

YONKERS, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE REACTION OF ORGANIC MERCURY COMPOUNDS WITH ORGANIC HALIDES. II[1]

BY FRANK C. WHITMORE AND E. N. THURMAN

RECEIVED NOVEMBER 21, 1928 PUBLISHED MAY 6, 1929

The present research was undertaken to study the failure of organic halides to react "metathetically" with organic mercury compounds to give lengthened carbon chains according to the equations

$$R_2Hg + R'X \longrightarrow R{-}R' + RHgX$$
$$RHgX + R'X \longrightarrow R{-}R' + HgX_2$$

The original attempt at such a reaction was partly successful.[2] Mercury diphenyl heated with benzal chloride at 150° without a solvent gave some triphenylmethane. Almost all later attempts to extend this reaction have failed. These attempts have been very scattering and no systematic study of the reaction has been made.[3]

For the present study it was decided to treat a representative variety of organic halides with a single mercury compound under comparable conditions to determine the ease of reaction and the nature of the products formed. It seemed best to use an aromatic mercury compound for the following reasons: (1) aromatic mercury compounds being only slightly volatile are less dangerously poisonous, (2) they are more stable toward heat and (3) they give products more easily identified. The most readily available compound was mercury di-*p*-tolyl.[4] In one case mercury di-*n*-butyl was also used. After the projected study had been completed, work appeared which could be interpreted as indicating mercury diphenyl

---

[1] Presented at the First National Symposium on General Organic Chemistry, Rochester, New York, December, 1925. Whitmore and Thurman, THIS JOURNAL, 45,1068 (1923).

[2] Kekulé and Franchimont, *Ber.*, 5, 907 (1872).

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, pp. 79-83.

[4] Whitmore, Frances Hamilton and Thurman, THIS JOURNAL, 45, 1066 (1923).

to be much more reactive than mercury ditolyl.[6] Consequently, several of the reactions have been repeated with mercury diphenyl by F. L. Carnahan of this Laboratory. Mercury diphenyl was found to be only slightly more reactive than mercury ditolyl in the cases studied.

The mercury ditolyl proved to be extraordinarily unreactive in about half the cases studied. When reactions took place, the peculiarities of the mercury compound were found to differ only in degree from those of other types of bases in their reactions with organic halides. A thorough search of the literature showed that the types of bases represented by sodium hydroxide, sodium amide, sodium methylate, sodium hydride and sodium methyl, namely, aquo, ammono, alcoholo, hydro and hydrocarbo bases, often fail to give the "metathetical" reactions which would be represented by the equation

$$RX + MB \longrightarrow RB + MX \qquad (I)$$

in which R is any organic radical, X is a halogen, M is a metal and B is a "basic" radical such as hydroxyl, amino, methoxyl, negative hydrogen or methyl.

A much more general reaction with all types of bases is the removal of halogen acid to form an ethylenic linkage according to the equation

$$R_2CXCHR_2 + MB \longrightarrow R_2C{=}CR_2 + MX + HB \qquad (II)$$

in which the R's represent hydrogen atoms and organic radicals. A special case of the removal of halogen acid is given by the equation

$$2R_2CHX + 2MB \longrightarrow R_2C{=}CR_2 + 2MX + 2HB \qquad (III)$$

The "metathetical" reactions illustrated by Equation I probably consist in the union of the two free radicals liberated by the union of M and X to form a salt, MX. Sometimes when hydrocarbo bases are used the similar radicals combine according to the equation

$$2RX + 2MR' \longrightarrow R{-}R + R{-}R + 2MX \qquad (IV)$$

Another possibility with hydrocarbo bases is the disproportionation of the free radicals to form saturated and unsaturated compounds.

$$R_2CHCH_2X + MCH_2CHR_2 \longrightarrow R_2CHCH_3 + R_2C{=}CH_2 + MX \qquad (V)$$

Another type of reaction given by hydrocarbo bases but not by aquo, ammono or alcoholo bases is the removal of two halogen atoms from adjacent carbon atoms.

$$R_2CXCXR_2 + MR \longrightarrow R_2C{=}CR_2 + RX + MX \qquad (VI)$$

In this case R may also be hydrogen or even halogen.

In certain rare cases the metal takes the place of the halogen, $RX + MB \longrightarrow MR + BX$. Usually BX is a very reactive substance capable of reacting with another molecule of MB. The net reaction thus becomes

$$RX + 2MB \longrightarrow RM + B{-}B + MX \qquad (VII)$$

---

[5] Calvery, THIS JOURNAL, 48,1009 (1926).

The organic mercury compounds studied with various halides were found to give the reactions represented by Equations I, II, III and VI. The surprising fact noted in most of the work was the very slight reactivity of the mercury compounds with halides. In most cases it was necessary to heat the solutions at 110° for about **300** hours to bring about the reactions. Even under such drastic conditions more than half of the halides failed to react and were recovered unchanged.

The general procedure was to reflux the halide with an excess of the mercury compound in dry toluene solution for about **300** hours or until reaction had taken place. In a few cases, in which a lower boiling solvent seemed desirable, carbon tetrachloride or chloroform was used.

Of the thirty-two organic halides studied eighteen gave no perceptible reaction even after refluxing for **300–350** hours in dry toluene with an excess of mercury di-p-tolyl. In these cases the mercury compounds and the halide were recovered unchanged. The mercury compound was in each case tested qualitatively for halogen to see if any *p*-tolylmercuric halide had been formed, thus indicating some reaction. The mercury ditolyl was free from halogen in each case.

The halides which gave no reaction with mercury di-p-tolyl on refluxing in toluene for **300–350** hours may be classified as follows: alkyl halides (*sec.*-butyl iodide, lauryl bromide), alicyclic halide (cyclohexyl bromide), unsaturated halide (allyl iodide),[6] halogenated ketone (α-bromo-camphor), halogenated esters, (ethyl dibromo-acetate, methyl α-bromo-*iso*butyrate),[7] acid halide (benzoyl chloride),[8] polyhalogen aliphatic compounds (ethylidene chloride, ethylene dibromide, tetrachloro-ethane, hexachloro-ethane), halogenated ethers (β-bromo-ethyl phenyl ether, γ-bromopropyl phenyl ether), toluene halogenated in the side chain (benzyl iodide, benzal chloride, benzo trichloride) and aromatic halide (*sym.*-trinitrophenyl iodide (picryl iodide)).[9]

[6] Carbon tetrachloride was used as solvent, as the temperature of boiling toluene decomposed the halide. No reaction took place after 120 hours' refluxing in carbon tetrachloride.

[7] No action was noticeable after refluxing in carbon tetrachloride solution for 336 hours. Refluxing for 300 hours in toluene solution appeared to give a slight reaction, as evidenced by the formation of a trace of tolylmercuric bromide.

[8] Benzoyl chloride was also refluxed with mercury diphenyl in dry benzene for 86 hours according to the directions of Calvery (ref. 5) except that an excess of the mercury compound was used. No benzophenone was obtained. The mercury diphenyl was recovered unchanged. The benzoyl chloride was unchanged. It was identified by conversion to the amide. The result of this experiment is in marked contrast to that obtained with an excess of the acid chloride.

[9] The statement appears in the literature, THIS JOURNAL, 43, 2243 (1921), that 2,4,6-trinitrophenylmercuric chloride reacts with iodine to give a mixture of picryl iodide and "presumably" hexanitrodiphenyl. This might be taken as an indication that picryl iodide reacts with the mercury compound to give hexanitrodiphenyl. An ex-

Six of the halides reacted with mercury ditolyl to give tolylmercuric halides and tarry products from which no other known substance could be isolated. These halides were bromonitromethane, which reacted completely on refluxing in carbon tetrachloride for 200 hours (shorter treatments gave no more satisfactory results); acetyl iodide, which reacted vigorously with mercury ditolyl at room temperature; dibenzoylbromomethane, w-bromo-acetophenone, phenyliodo-acetylene, iodo-acetonitrile. Two of the halides gave indefinite results and should be studied more fully. They were triphenylchloromethane and methyl α-bromo-*iso*butyrate (in toluene).

Ethyl bromomalonate reacted only partly with mercury ditolyl after refluxing in toluene for 336 hours. A considerable amount of tolylmercuric bromide was formed. The other substances found included unchanged ethyl bromomalonate, ethyl malonate, p-tolyl bromide and a small amount of an unidentified ester boiling at 205–210° (8 mm.). Since these products were hard to explain, the experiment was repeated on a larger scale using 100 g. of the ester and 335 g. of the mercury compound. The same products were obtained. The products separated accounted for 91% of the starting materials.

Five of the halides gave definite reactions. These correspond to four of the general types of reactions given by halides with the various classes of bases.

Reaction I. "Metathesis."—Diphenylbromomethane reacted with mercury di-*p*-tolyl on refluxing in toluene solution for 200 hours to give an 80% yield of diphenyl-*p*-tolylmethane. The same product was obtained when the reaction was repeated using pure m-xylene as solvent. This result showed that the solvent did not react with any free radical formed in the reaction. When mercury diphenyl was substituted for the tolyl compound, triphenylmethane was obtained in 90% yield. When mercury di-n-butyl was used, the products after refluxing for 340 hours were n-butylmercuric bromide, metallic mercury, a trace of mercurous bromide, a little tetraphenylethane and a 35% yield of diphenyl-*n*-butylmethane. The metallic mercury was due to the thermal decomposition of the mercury dibutyl, and the tetraphenylethane resulted from the action of mercury on the original bromide. These reactions were confirmed by side experiments.

The reaction of diphenylbromomethane with organic mercury compounds is as follows

$$(C_6H_5)_2CHBr + R_2Hg \longrightarrow R(C_6H_5)_2CH + RHgBr$$

---

periment showed that these substances do not react with each other. Consequently, the original experiment was repeated. It was found that iodine reacts normally with both 2,4,6-trinitrophenylmercuric chloride and the corresponding mercuri-*bis* compound. In the latter case 66% alcohol had to be used as a solvent instead of water. Picryl iodide was formed in both cases. No hexanitrodiphenyl was found.

This halide reacts similarly with other types of bases. Alcoholic potassium hydroxide gives the ethyl ether of benzhydrol.[10] It also reacts "metathetically" with methyl- and ethylmagnesium bromides, giving the corresponding diphenylalkylmethanes.[11] It reacts with *p*-tolylmagnesium bromide to give good yields of *p*-tolyldiphenylmethane.[12]

Reaction II. Removal of HX.—*Tert.*-butyl bromide reacted almost quantitatively with mercury di-p-tolyl in carbon tetrachloride after refluxing for 340 hours. The products were tolylmercuric bromide, toluene and *iso*butylene. Mercury diphenyl gave similar results but seemed to react slightly more rapidly than the tolyl compound.

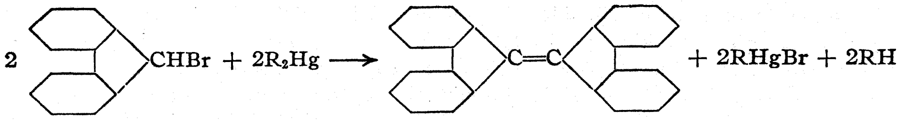
Tert.-amyl iodide gave similar results with mercury ditolyl and mercury diphenyl. When an excess of the iodide was used with mercury ditolyl, the products were mercuric iodide, toluene and trimethylethylene.

The tertiary halides react as follows

$$R_2CXCH_2R + R_2'Hg \longrightarrow R_2C{=}CHR + R'HgX + R'H$$

Tertiary halides react with other types of bases to give olefins.[13] These reactions differ from those with the mercury compounds in giving some of the "metathetical" product as well as the olefin. A similar reaction was obtained with mercury ditolyl and 1-bromo-1,1,2-tricarbethoxyethane, $(C_2H_5O_2C)_2C{=}CHCO_2C_2H_5$, being formed.

Reaction III. Removal of HX through "Methylene Dissociation."--Diphenylenebromomethane (9-bromofluorene), although it differs so slightly from diphenylbromomethane, reacts entirely differently with bases. After refluxing with mercury ditolyl and mercury diphenyl in toluene for 300 hours, the products isolated were the aryl mercuric bromides and *bis*-diphenylene ethylene.



To make sure that the mercury compound was necessary for the formation of the ethylene compound, 9-bromofluorene was refluxed alone in toluene for 120 hours. The halide was recovered unchanged. 9-Bromofluorene gives an entirely similar reaction with alcoholic potassium hydroxide.[14]

Reaction VI. Removal of Bromine.—Stilbene dibromide reacts with

---

[10] Nef, *Ann.*, 298, 202 (1897).

[11] Späth, *Monatsh.*, 34, 1965 (1915).

[12] Boudroux, *Bull. soc. chim.*, [4] 17,318 (1915); *Ann. chim.*, [9] 5, 580 (1916).

[13] Aquo and alcohol bases. Lazinsky and Swodkowsky, *Chem. Zentr.*, I. 1119 (1903); Nef, *Ann.*, 309, 1381 (1899); Kindakow, J. *Russ. Phys.-Chem. Soc.*, 19, 301 (1887); Beilstein-Priiger-Jacobson, 4th ed., Vol. I, p. 138. Hydrocarbo bases: Späth, *Monatsh.*, 34, 1965 (1913); Markownikoff, *Ber.*, 32, 1445 (1899); 33, 1905 (1900); Steinkopf, *Ann.*, 413,315 (1916).

[14] Thiele, *ibid.*, 211, 1 (1896); 376,278 (1910).

mercury ditolyl after refluxing in toluene for 340 hours to give the tolylmercuric bromide, tolyl bromide and stilbene.

$$C_6H_5CHBrCHBrC_6H_5 + 2R_2Hg \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2RBr + 2RHgBr$$

The tendency of stilbene dibromide to lose bromine is shown by its reactions with a number of other basic substances. Phenylmagnesium bromide gives stilbene and diphenyl.[15] Sodium malonic ester gives a quantitative yield of stilbene and ethane-tetracarboxylic ester.[16] Potassium sulfhydrate in a sealed tube at 100° gives large quantities of stilbene.[17] Sodium benzene sulfinate and sodium phenylmercaptide give stilbene and diphenylsulfone and diphenyl disulfide, respectively.[18] On the other hand, stilbene dibromide does not react with sodium ethylate, with alcoholic ammonia or with aniline and only slightly with metallic sodium. With alcoholic potassium hydroxide at room temperature it loses a molecule of hydrogen bromide and forms monobromostilbene.[19]

A study of the reactions of mercury di-*p*-tolyl and of mercury diphenyl with organic halides shows that they are far less reactive than the other types of bases. The use of higher temperatures and the omission of solvents would probably speed up the reactions appreciably. Most of the halides used would not withstand such severe conditions, however. When mercury compounds can be made to react with organic halides, the results are reasonably like those obtained with other types of bases, especially those of the hydrocarbo type.

Experimental Part

Only a few typical experiments will be given in detail to indicate the method of procedure.

Reaction of *sec.*-Butyl Iodide with Mercury Di-*p*-tolyl.—A mixture of 3.5 g. (1 mol) of *sec.*-butyl iodide (b. p. 119–122°), 12 g. (2 mols) of mercury ditolyl and 50 cc. of dry carbon tetrachloride (b. p. 76–77°) was refluxed for 380 hours. The condenser was provided with a trap containing bromine to absorb any unsaturated gaseous products. After refluxing, the contents of the trap were entirely soluble in dilute sodium hydroxide. This indicated that no butylene had been formed. The mixture was cooled and filtered. The precipitate of unchanged mercury ditolyl was washed with carbon tetrachloride and dried (wt., 10.4 g.). A sodium fusion test for halogen gave only a Slight opalescence, showing that not more than a trace of tolylmercuric iodide was formed.

The filtrate was concentrated to about 10 cc., cooled and filtered from more mercury ditolyl. Most of the filtrate distilled at 76–80°. Finally, unchanged butyl iodide distilled at 117–122°. No reaction had occurred

The experiment was repeated with the same weights of material in boiling toluene for 340 hours. No reaction occurred.

---

[15] Kohler and Johnstin, *Am.* Chem. **J., 33,** 42 (1905).

[16] Bischoff, Ber., 21, 2071 (1888).

[17] Auwers, *ibid.*, 24, 1779 (1891).

[18] Otto, J. prakt. Chem., [2] **33, 3** (1896).

[19] Wislicenus, Ber., 28, 2699 (1895).

Table IA

Other Halides which Gave no Reaction with an Excess of Mercury Di-*p*-tolyl

No.	Halide	G.	Hg cpd , g.
1	Lauryl bromide, $CH_3(CH_2)_{10}CH_2Br$, b. p. 185–187° (45 mm.)	8	24
2	Ethylidene chloride, CH_3CHCl_2, b. p. 56–58"	23	22.8
3	Ethylene bromide, CH_2BrCH_2Br, b. p. 130–132°	3	12
4	Tetrachloro-ethane, $CHCl_2CHCl_2$, b. p. 144–146°	4	18
5	Hexachloro-ethane, CCl_3CCl_3, m. p. 185–186"	3	8.7
6	Allyl iodide, $CH_2{=}CHCH_2I$, b. p. 101–103°	3 5	13.8
7	Benzyl iodide,[b] $C_6H_5CH_2I$, m. p. 27–30'	5	17.5
8	Benzal chloride, $C_6H_5CHCl_2$	10	47
9	Benzo trichloride, $C_6H_5CCl_3$, b p. 212–214°	4	15 6
10	Cyclohexyl bromide, $C_6H_{11}Br$, b. p. 59–60" (10 mm.)	20	94
11	β-Bromo-ethylphenyl ether, b. p. 125-130" (20 mm.)	20	76
12	γ-Bromopropylphenyl ether, b. p. 127" (18 mm.)	20	70
13	Benzoyl chloride, C_6H_5COCl, b. p. 197°	3	16 2
14	Benzoyl chloride, C_6H_5COCl, b. p. 197°	3.5	109 .0[a]
15	Ethyl dichloro-acetate, $Cl_2CHCOOC_2H_5$, b. p. 150–154°[c]	4	19.6
16	Methyl α-bromo-*iso*butyrate,[d] $(CH_3)_2CBrCOOCH_3$, b. p. 67° (37 mm.)	15	63
17	a-Bromocamphor, m p. 75°	10	33
18	*Sym.*-trinitrophenyl iodide, m. p. 159–160°	5.3"	3
19	*Sym.*-trinitrophenyl iodide, m. p. 159–160°	5.3	3

[a] Mercury diphenyl was used in this experiment.

[b] The benzyl iodide was prepared by the action of benzyl chloride with sodium iodide in absolute methyl alcohol. The product was freed from alcohol by standing in a vacuum desiccator over solid potassium hydroxide for two weeks A trace of free iodine was removed by shaking the melted iodide with a little mercury. The product was almost colorless and melted at 27–30°.

[c] No product obtained with a boiling point appreciably higher than those of the solvent and the halide.

[d] When the reaction was carried out in toluene considerable tolylmercuric bromide was formed. The methyl ester of a-methylacrylic acid, which may have been formed, was not detected.

[e] In this experiment the molar ratio of halide to mercury compound was 2.1 instead of the ratio 1:2 used in the other experiments.

Table IB

Experimental Data

No.	Dry toluene, cc.	Refluxing, hours	Hg cpd. recov , g.	Halide recovered, g.	Remarks
1	60	240	23.4	6 b. p. 151–153° (20 mm.)	No dodecylene
2	125"	360	20.7	. . .	[b]
3	50	350	11.1	1.1 b. p. 130°	[b,c]
4	70	340	14.8	B. p. 135°	[b,c]
5	50	385	6 8	2 m. p. 176–181°	Trace of metallic Hg
6	50"	120	[d]	2.5 b. p. 95–101°	[b,c]
7	100	236	. .	2.4 b. p. 105–107° (20 mm.)	[e]
8	250	336	. .	. . .	[b]
9	60	336	. .	3 b. p. 190–200°	[b]
10	250	335	92.3	. . .	No cyclohexene[b]

TABLE IB (Concluded)

No.	Dry toluene, cc.	Refluxing, hours	Hg cpd. recov., g.	Halide recovered, g.	Remarks
11	200	336	74.2	16.7 b. p. 125–127° (24 mm.)	. .
12	200	336	. .	16 b. p. 135–137° (19 mm.)	. .
13	85	288	. .	B. p. 146–187°	[b]
14	100	85[f]	7.4	. . .	[b]
15	85	336	. .	B. p. 155–160°	[b]
16	200"	430	62	12	. .
17	125	336	31.3	6.5 b. p. 140–147° (29 mm.) M. p. 74°	Metallic Hg (1.5 g.)[b]
18	100"	75	M. p. 235–238°	M. p. 162–164°	No HgI_2 formed
19	100	66	4.5	2	Dark tar, 1 g. No HgI_2

[a] Dry carbon tetrachloride was used as solvent in this experiment.

[b] No product obtained with a boiling point appreciably higher than those of the solvent and the halide.

[c] Bromine trap used. Contents entirely soluble in dilute sodium hydroxide, indicating that no olefin was formed during the refluxing.

[d] In some of the earlier experiments the recovered mercury ditolyl was not dried and weighed.

[e] The condenser was protected from moisture by a calcium chloride tube.

[f] Dry benzene was used as solvent in this experiment.

The next group of halides to be discussed reacted with mercury ditolyl but gave tarry products which could not be purified.

TABLE II

REAGENTS AND PRODUCTS

Halide	G.	Hg compd., g.	Dry solvent, cc.
Bromonitromethane, $BrCH_2NO_2$, b. p. 146–147"	25	125	250"
Acetyl iodide, CH_3COI, b. p. 100–102°	20	90	400[b]
Bromo-acetophenone, $C_6H_5COOCH_2Br$	10	38	150"
Bromo-acetophenone, $C_6H_5COOCH_2Br$	10	38	200[a]
Dibenzoylbromomethane, $(C_6H_5CO)_2CHBr$	5	12.3	50[c]
Phenyliodo-acetylene, $C_6H_5C{\equiv}CI$	8[d]	3.5	50[c]
Iodo-acetonitrile, ICH_2CN	20	92	300"

[a] Dry carbon tetrachloride. [b] Dry chloroform. [c] Dry toluene. [d] The molar ratio of halide to mercury in this experiment was 1:1 instead of the usual 1:2.

TABLE IIB

TIMES, PRODUCTS AND REMARKS

Refluxing, hours	Products identified	Remarks
200	C_7H_7HgBr	Tarry oil, 26 g. No unchanged $BrCH_2NO_2$
200[a]	C_7H_7HgI, HI and I_2	Black tar, 4 g.
336	C_7H_7HgBr, 1.5 g. of Hg	No odor; 10.5 g "shellac," 1 g. of substance, m. p. 86–95"
240	Unchanged materials	Odor and lachrymation
70	C_7H_7HgBr	Tar, 7 g. Crystals, 0.2 g., m. p. 120–122°
44	HgI_2, C_7H_7HgI	Red gum. No $C_6H_5{\equiv}CCI$
310	C_7H_7HgI, 6 g. ICH_2CN	Tar

[a] The mixture was allowed to stand at room temperature (about 20°).

Reaction of Ethyl Bromomalonate with Mercury Di-*p*-tolyl.—A mixture of 100 g. (1 mol) of ethyl bromomalonate (b. p. (20 mm.) 130–132°), 335 g. (2 mols) of mercury di-*p*-tolyl (m. p. 235–239°, free from iodide) and 950 cc. of dry toluene was refluxed for 336 hours. The mixture was cooled and filtered from a mixture of unchanged mercury ditolyl and tolylmercuric bromide. This was dried; wt., 300 g. The filtrate was concentrated by distillation to 400 cc. (b. p. of distillate 110–115°). The residual oil gave more of the mixed mercury compound on cooling. This was removed by filtration and dried; wt., 9 g. The filtrate was further concentrated to 150 cc. and filtered from more of the mercury compound; wt., 6 g. This filtrate was distilled at 58–60 mm. Toluene first came over at 44–55°. The temperature then rose rapidly to 125° and then more slowly to 149°. About half of the oil distilled at 140–149° (58–60 mm.). The liquid was water white; wt., 56 g. When the temperature was carried above 150°, considerable mercury ditolyl began to distil. The heating was then stopped. The residual oil solidified to a mush of brown crystals; wt.. 42 g.

The oil which distilled at 140–149° (58–60 mm.) was distilled at 38–40 mm. Three fractions were obtained as follows: b. p. 100–116° (mostly 107–116°), wt. 18 g.; b. p. 115–130° (mostly 123–127°), wt. 10.7 g.; b p. 137–145°, wt. 23 g. About 3 g. of charred residue remained in the flask.

The first fraction was redistilled at atmospheric pressure. It boiled at 180–205° (mostly at 190–195°, b. p. of ethyl malonate 198°). The entire fraction (16 g.) was treated with 40 cc. of concd. ammonium hydroxide. Part of the material was insoluble and this was separated; wt., 4 g. (b. p. 183–185°). It gave a qualitative test for bromine and had the characteristic odor of p-bromotoluene. The ammoniacal solution deposited white crystals on evaporation, m. p. 168–169°. A mixture with pure malonamide (m. p. 170–171°) melted at 169–171°.

The third fraction was unchanged ethyl bromomalonate, as shown by its b. p. and by conversion into 1,1,2,2-tetracarbethoxyethylene. Two g. of the oil, 6 g. of anhydrous potassium carbonate and 25 cc. of benzene were refluxed for twenty-four hours. The product melted at 55–57°. The melting point was not lowered by the addition of a known sample of the ester melting at 58°.

The second fraction was not separated into its components. It undoubtedly contained ethyl malonate, ethyl bromomalonate and @-bromotoluene.

The 42 g. of residue from the first distillation was too viscous to be filtered. Repeated extractions with alcohol left a residue of impure mercury ditolyl; wt., 20 g. After one crystallization from benzene it melted at 226–238'. The alcohol extracts gave a thick, viscous oil which contained organic mercury compounds. An attempt to distil this at 8-mm. pressure was only partly successful. There was much charring in the flask. About 10 g. of oil distilled at 195–230° (8 mm.), mostly at 205–210°. It contained some mercury ditolyl and tolylmercuric bromide in suspension. The liquid portion was perhaps 1,1,2,2-tetracarbethoxyethylene, b. p. 201° (2 mm.).

Reaction of Diphenylbromomethane and Mercury Di-*p*-tolyl.—Preliminary experiments using carbon tetrachloride, toluene, xylene and tetrachloro-ethane as solvents showed that a reaction took place.

A mixture of 50 g. (1 mol) of diphenylbromomethane (b. p. 180–182° (17 mm.), m. p. 40–42°), 120 g. (2 mols) of mercury di-p-tolyl and 250 cc. of dry toluene was refluxed for 170 hours. The mixture was cooled and filtered from 110 g. of mixed mercury compounds. The filtrate was concentrated to 75 cc. by distillation, cooled and filtered from 5 g. of mercury compounds. The filtrate was freed from toluene by distillation. The residual oil (wt., 43 g.) solidified on cooling. It gave no test for bromine (sodium fusion). Recrystallization from alcohol gave white needles, m. p. 64–66°. Part of the material was distilled at atmospheric pressure, b. p. above 360°. The distillate solidified and melted at 70°. The melting point was not lowered by mixing with a known sample of p-tolyldiphenylmethane (m. p. 71°) made from benzhydrol and toluene with stannic chloride. The product was further identified by oxidation to form *p*-carboxytriphenylcarbinol, m. p. 196–200°.[20]

Reaction in *m*-**Xylene.**—A mixture of 47 g. (1 mol) of diphenylbromomethane, 117.5 g. (2 mols) of mercury di-p-tolyl and 400 cc. of m-xylene (Eastman Kodak Co., b. p. 138–139°) was refluxed for 200 hours. The mixture was treated as in the preceding experiment. The crude p-tolyldiphenylmethane boiled at 225–232° (18 mm.). The distillate on recrystallization from a mixture of acetic acid and ether melted at 68–78°. The melting point was not lowered by addition of some of the known compound. No evidence of the formation of m-xylyldiphenylmethane was found.

Reaction of Diphenylbromomethane with Mercury **Di-*n*-butyl.**—A mixture of 20 g. (1 mol) of the halide, 50 g. (2 mols) of mercury di-n-butyl (b. p. 225–230°) and 100 cc. of dry toluene was refluxed for 340 hours. The top of the condenser was connected with a flask of concd. nitric and sulfuric acids to destroy any traces of organic mercury compounds which might escape from the condenser. The reaction mixture was separated as usual. The products obtained were 5 g. of metallic mercury, 15 g. of unchanged mercury di-n-butyl, 25 g. of n-butylmercuric bromide, 2 g. of mercurous bromide, 2 g. of tetraphenylethane and 6 g. of oil boiling at 277–278° (probably diphenyl-*n*-butylmethane).

Reaction of Diphenylbromomethane with Mercury.—Two g. of the halide, 15 g. of metallic mercury and 20 cc. of dry toluene were refluxed for twenty-four hours. The hot solution was filtered from a residue of mercury and mercurous bromide. On cooling it deposited white crystals of *sym.*-tetraphenylethane, m. p. 208–209° corr.; wt., 1 g. The melting point was not lowered by addition of known tetraphenylethane made from diphenylbromomethane and zinc dust.

Reaction of Diphenylbromomethane with Mercury **Diphenyl.**—A mixture of 10 g. (1 mol) of diphenylbromomethane, 21.72 g. (2 mols) of mercury diphenyl and 50 cc. of dry toluene was refluxed for 170 hours. The mixture was allowed to cool and the precipitated mercury compounds were filtered off and washed with a little toluene and dried; wt., 15 g. The filtrate was concentrated in *vacuo.* The residue solidified on cooling; wt., 15 g. Extraction with petroleum ether (b. p. 30–60°) left 6 g. of mixed mercury compounds. The soluble portion was found to be triphenylmethane. It crystallized from petroleum ether on standing, m. p. 85–90°. Recrystallization from petroleum ether raised the melting point to 88–90°. (Melting point of triphenylmethane, 92°.) The identity of the material was further established through the test given by Mulliken.[21] The material was nitrated by dissolving 0.1 g. in fuming nitric acid without the application of heat. The mixture was diluted with water and the precipitate filtered off. The precipitate was dissolved in 10 cc of glacial acetic acid and reduced by the successive additions of small quantities of zinc dust to the hot solution until the strong red color that at first appeared was nearly discharged. A portion of the supernatant Liquid was decanted and a little lead dioxide added. A very intense fuchsin-red colot (pararosaniline) formed at once, indicating that the substance tested was triphenylmethane. The yield of triphenylmethane was about 90%.

Reaction of *tert.*-**Butyl** Bromide with Mercury **Di-*p*-tolyl.**—1. A mixture of 10 g. (1 mol) of *tert.*-butyl bromide (b. p. 72–74°), 55 g. (2 mols) of mercury di-p-tolyl and 200 cc. of dry carbon tetrachloride was refluxed for 340 hours. The top of the con-

---

[20] Bistrzycki and Gyr, Ber., 37,657 (1904).

[21] Mulliken, "Identiiication of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. 177.

denser was connected with a trap containing 85% sulfuric acid. After twenty-four hours an oily layer separated above the acid. This was probably tri-isobutylene.

The reaction mixture was cooled and filtered from 53 g. of a mixture of unchanged mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 90 cc. by distillation (b. p. 76–77"). The residue was cooled and filtered from 0.5 g. of mercury compounds. It was further concentrated to 15 cc. (b. p. of distillate, 76–80°). Cooling gave 0.5 g. more mercury compounds. The filtrate on distillation gave 10 cc. of product boiling at 80–110°. The temperature then rose rapidly to 155°, at which point charring took place. Less than 1 cc. of high-boiling oil was obtained. Treatment of the main distillate with fuming sulfuric and nitric acids proved the presence of toluene. The melting point of the nitration product was 69–70' (m. p. of 2,4-dinitrotoluene, 70.5").

2. The experiment was repeated using 66% sulfuric acid in the trap. No oily layer separated. At the end of 200 hours the contents of the trap was neutralized with sodium hydroxide and distilled. The distillate gave the red ring test for *tert.*-butyl alcohol.[22] This proved that isobutylene was formed in the reaction.

Reaction of *tert.*-Butyl Bromide with Mercury Diphenyl.—A mixture of 5 g. (1 mol) of *tert.*-butyl bromide, 24.9 g. (2 mols) of mercury diphenyl and 100 cc. of dry carbon tetrachloride was refluxed for 340 hours. A trap containing 70% sulfuric acid was used to catch any unsaturated gases. The reaction mixture was cooled and filtered from 12 g. of mercury compounds. The filtrate was distilled (75–81°), leaving a residue of 15 g. of mercury compounds in the flask. The distillate on treatment with fuming nitric and fuming sulfuric acids gave m-dinitrobenzene melting at 88–89°. The sulfuric acid in the trap was diluted with water and neutralized with sodium hydroxide solution. It gave the test for *tert.*-butyl alcohol, indicating that isobutylene had been formed.

Reaction of *tert.*-Amyl Iodide with Mercury Di-*p*-tolyl.—A mixture of 6.5 g. (2 mols) of the iodide, 6.3 g. (1 mol) of the mercury compoand and 45 cc. of dry carbon tetrachloride was refluxed for seventeen hours. Red crystals of mercuric iodide separated. The cooled mixture was filtered from 7.2 g. of mercuric iodide and tolylmercuric iodide. Distillation of the filtrate gave 3 cc. of a product boiling at 83–113°. This was mainly toluene, as was proved by conversion to dinitrotoluene (m. p. 68–70"). A small amount of unchanged amyl iodide was recovered.

Reaction of *tert.*-Amyl Iodide with Mercury Diphenyl.—A mixture of 6.5 g. (2 mols) of *tert.*-amyl iodide, 5.7 g. (1 mol) of mercury diphenyl and 45 cc. of chloroform was refluxed for seventeen hours. A trap containing 70% sulfuric acid was used to catch any volatile unsaturated compounds. The mixture of unchanged mercury diphenyl and phenylmercuric iodide left weighed 5.4 g. The contents of the trap gave a small amount of *tert.*-amyl alcohol. Benzene was identified as m-dinitrobenzene (m. p. 88–89'). A small amount of the amyl iodide was recovered unchanged. No mercuric iodide was formed.

Preparation of 1-Bromo-1,1,2-tricarbethoxyethane (Bromo-ethenyltricarboxylic Ester).—Ethenyltricarboxylic ester was prepared from ethyl chloro-acetate and sodium malonic ester. It boiled at 163–165° (17 mm.). It was brominated without a solvent. The bromo ester boiled at 175–177° (15 mm.); yield, 76%.

Anal. Subs., 0.4092, 0.3565: AgBr, 0.2348, 0.2032 Calcd. for $C_{11}H_{17}O_6Br$: Br, 24.6. Found: Br, 24.3, 24.4.

Reaction of 1-Bromo-1,1,2-tricarbethoxyethane with Mercury Di-*p*-tolyl.—A mixture of 25 g. (1 mol) of the ester, 58.8 g. (2 mols) of the mercury compound and 200 cc. of dry toluene was refluxed for 288 hours. The reaction mixture was dark brown and a small globule of mercury had appeared. The cooled mixture was filtered to

---

[22] Mulliken, ref. 21, Vol. I, p. 171.

separate 48.2 g. of mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 25 cc. (b. p. of distillate mostly 110–112', a little up to 120'). The residue on cooling gave 4.8 g. of mixed mercury compounds. The filtrate freed from solvents weighed 16 g. It was twice distilled at 12-mm. pressure. A small amount was obtained which boiled at 157–159° (12 mm.). This was 1,1,2-tricarbethoxyethylene (ethenetricarboxylic ester).[23]

Reaction of 9-Bromofluorene with Mercury **Di-*p*-tolyl.**—A mixture of 4 g. (1 mol) of the halide (m. p. 102–103°), 12.4 g. (2 mols) of the mercury compound and 60 cc. of dry toluene was refluxed for 310 hours. The cooled mixture was filtered, leaving 11.1 g. of mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 10 cc. (b. p. of distillate 109–112") and cooled. It was filtered from 1.1 g. of mixed mercury compounds. The filtrate was evaporated to a tarry mass; wt., 3 g. This was dissolved in benzene and treated with a concd. benzene solution of picric acid. On spontaneous evaporation beautiful crystals of the picrate of *bis*-diphenylene-ethylene separated, m. p. 176–177°.

Action of Heat on **9-Bromofluorene.**—Three g. of the halide and 25 cc. of dry toluene were refluxed for 120 hours. The original bromide was recovered unchanged. No trace of the orange ethylene compound was noted.

Reaction of 9-Bromofluorene with Mercury **Diphenyl.**—A mixture of 4 g. (1 mol) of the halide, 11.2 g. (2 mols) of mercury diphenyl and 60 cc. of dry toluene was refluxed for 238 hours. The mixture turned deep orange. It was cooled and filtered from the mixed mercury compounds. The toluene was distilled and the residue was extracted with petroleum ether (b. p. 30–60°). Evaporation of the solvent left an orange red oil which consisted mainly of bis-diphenylene-ethylene.

Reaction of Stilbene Dibromide with Mercury **Di-*p*-tolyl.**—A mixture of 4 g. (1 mol) of the halide (m. p. 226–229°), 10 g. (2 mols) of the mercury compound and 70 cc. of dry toluene was refluxed for 340 hours. The mixture was cooled and filtered from unchanged mercury ditolyl and tolylmercuric bromide. The toluene was removed by distillation in *vacuo*. The residue was extracted with absolute ethyl alcohol. Evaporation of the extracts gave crystals of m. p 103–115"; recrystallization from ligroin raised the m. p. to 113–115°. This was impure stilbene. Bromination of a sample gave stilbene dibromide, m. p. 224–225°. A small amount of oil having the odor of p-bromotoluene was obtained from the mother liquors of the crude stilbene.

Treatment of Mercuri-*bis*-2,4,6-trinitrophenyl with Picryl Iodide.—One g. (1 mol) of the mercury compound[24] (m. p. 271°), 1.1 g. (2 mols) of picryl iodide and 25 cc. of acetone were refluxed for nineteen hours. The mixture was evaporated spontaneously. Nothing but the original substances could be found in the mixture.

Reaction of 2,4,6-Trinitrophenylmercuric Chloride with Iodine.—One g. (1 mol) of the mercury compound, 0.6 g. (1 mol) of iodine, 4.5 g. of sodium iodide and 25 cc. of water were refluxed for two hours. The mixture was filtered. The residue was completely soluble in ether, m. p. 164°. The melting point was not lowered by addition of picryl iodide. The filtrate contained sodium mercuric iodide, sodium iodide and sodium chloride. No hexanitrodiphenyl was formed.

Reaction of Mercuri-*bis*-2,4,6-trinitrophenyl with Iodine.—A mixture of 0.6 g. (1 mol) of the mercury compound, 0.6 g. (2.2 mols) of iodine and 30 cc. of 66% alcohol was refluxed for eight hours. Practically all of the iodine had reacted. Less than 0.1 g. of unchanged mercury compound was recovered. Evaporation gave needles of picryl iodide melting at 162–163°. A mixture with the known substance melted at 162–164". The other product was mercuric iodide.

---

[23] Ruhemann and Cunnington, *J. Chem.* Soc., 73, 1012 (1898).

[24] Kharasch, This Journal, 43, 2242 (1921).

Summary

1. Thirty-two organic halides of widely varying types have been treated with mercury di-p-tolyl under very vigorous conditions.
2. Some of the halides have also been treated with mercury di-n-butyl sod mercury diphenyl.
3. In general the mercury compounds are extraordinarily unreactive toward the halides studied.
4. In the cases of the five halides which gave definite reactions the behavior of the mercury compounds was analogous to that of other types of bases with the same halides.
5. It has been shown that 2,4,6-trinitrophenylmercuric compounds react normally with iodine.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

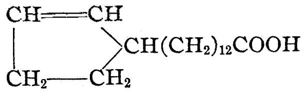
NEW PHENOLIC COMBINATIONS OBTAINED BY COUPLING CHAULMOOGRIC ACID WITH RESORCINOL[1]

BY W. S. HINEGARDNER[2] AND TREAT B. JOHNSON

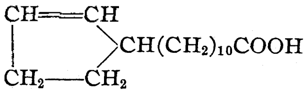
RECEIVED DECEMBER 5, 1928 PUBLISHED MAY 6, 1929

Chaulmoogric (I) and hydnocarpic (II) acids[3] in the form of their salts and esters are extensively used in leprosy therapy.[4] Notwithstanding the fact, however, that many cures have been effected through their application, many objections have been raised to their prolonged therapeutic use, and there is still much to be desired before an ideal germicidal agent is found for the treatment of patients suffering from leprosy. New compounds of high germicidal power and low toxicity are very much desired for clinical work in the study of methods to eradicate this disease. In view of the striking bactericidal properties of alkylresorcinols and the established clinical success of hexylresorcinol[5] it seemed desirable to prepare

I



II



---

[1] Constructed from a dissertation presented by Wilbie S. Hinegardner to the Faculty of the Graduate School of Yale University, June, 1927, in candidacy for the degree of Doctor of Philosophy.

[2] Holder of the Richard Wrenshall Research Prize in 1925–1926.

[3] Barrowcliff and Power, *J. Chem. Soc.*, *91*, 557 (1907); Shriner and Adams, THIS JOURNAL, 47, 2727 (1925).

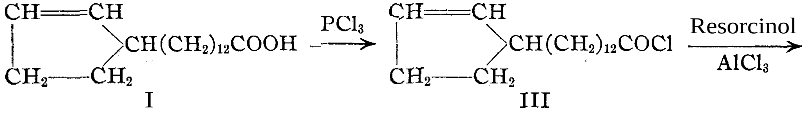
[4] Rogers, Brit. *Med. J.*, **4**, 550 (1916); 5, 277 (1917); McDonald and Dean, *J. Am. Med. Assoc.*, 76, 1470 (1921); Muir, *Indian J. Med. Research*, *11*, *543* (1923).

[5] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); Dohme, Cox and Miller, *ibid.*, 48,1688 (1926); V. Leonard, *Science*, 62, 408 (1925); Leonard and Feirer, *Surgery Gynecol. Obstet.*, 45, 603–611 (1927).

some resorcinol derivatives containing the cyclopentenyl group. As chaulmoogric acid was available[6] in quantity we have used it to prepare the first of this new type of compounds, namely, 1-cyclopentenyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane, V. It is a derivative of chaulmoogric acid containing no carboxyl or ester group, and thus differs structurally from those previously used in leprosy treatment. The method of synthesis reported in this paper should lend itself equally well to the preparation of lower homologs of the series; their investigation is in progress in this Laboratory.

We have introduced the chaulmoogryl group into the nucleus of resorcinol by application of the Friedel and Crafts reaction, using carbon disulfide as the solvent when the dimethyl ether of resorcinol was used, and nitrobenzene[7] when using resorcinol directly. The method developed by Nencki and others[8] of heating resorcinol and the acid in the presence of anhydrous zinc chloride was entirely inapplicable, the zinc chloride reacting with the unsaturated part of chaulmoogric acid giving resinous decomposition products. However, this latter method proved entirely satisfactory with dihydrochaulmoogric acid.[9] The preparation of resorcinol-monochaulmoograte and the rearrangement of the chaulmoogryl group into the resorcinol nucleus were not successful. The methyl group of dimethly-resorcinol para to the entering chaulmoogryl group could not be removed without complete breakdown of the compound. It has been recognized previously that methyl groups para to a ketone group are removed with difficulty, but when ortho to a ketone group they are removed with comparative ease.[10] Only those ketones in which the carbonyl is ortho to a phenol group give a red color with ferric chloride.

These ketones were readily reduced to the corresponding alkylresorcinols by the Clemmensen method.[11] The synthesis and reduction of chaulmoogryl resorcinol, IV, is represented by the following steps



---

[6] We wish to thank Dr. Richard Wrenshall of the University of Hawaii for supplying a large portion of the chaulmoogric acid used in this research. The remainder was obtained from chaulmoogra oil purchased in the market.

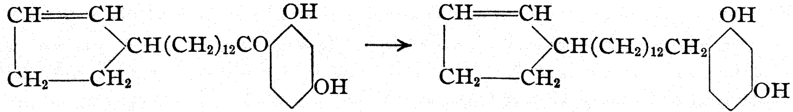
[7] Behn, *Chem. Zentr.*, I, 1223 (1898); German patent 95,901, *Friedlander,* 5, 143 (1900); Klarmann, THIS JOURNAL, 48, 2358 (1926); Bartlett and Garland, *ibid.*, 49, 2098 (1927).

[8] Nencki and Sieber, J. *prakt. Chem.*, 23, 147 (1881); Nencki and Schmid, *ibid.*, 23, 546 (1881); Nencki, *Monatsh.*, 10, 906 (1889).

[9] The dihydrochaulmoogricacid was kindly supplied to us by Dr. Richard Wrenshall.

[10] Auwers and Rietz, *Ber.*, 40, 3514 (1907).

[11] Clemmensen, *Ber.*, 46, 1837 (1913); 47, 51, 681 (1914); Johnson and Hodge, THIS JOURNAL, 35, 1014 (1913); Majima and Nakamura, *Ber.*, 46, 4089 (1913).



IV V

The double bond in the cyclopentenyl group is not reduced in this process since after reduction both the mono- and di-methyl ether of IV show optical activity. The non-optical activity of the 1-cyclopentenyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane, V, is probably due to internal compensation of the type shown by bromodihydrochaulmoogric acid, which is practically inactive though its esters show a decided optical activity.[12] The ketones which we have prepared show decreasing optical activity with decrease in methylation, and further decrease in optical activity upon reduction of the ketone group; thus it might be expected that V would show no measurable activity since the ketone IV is only slightly active.

1-Cyclopentyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane has been prepared and found to differ from 1-cyclopentenyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane, V, thus proving conclusively that the double bond in this compound is not reduced when it is treated according to the Clemmensen procedure. The great stability of the asymmetric carbon atom in chaulmoogric acid argues against racemization, and especially is this supported by the observation that the mono- and dimethyl ethers of the ketone, IV, show optical activity after reduction.

Experimental Part

Chaulmoogric Acid.—The chaulmoogric acid, which was brownish-yellow from slight oxidation, was distilled under 2–3 mm. pressure and crystallized once from ethyl acetate. Glistening white flakes melting at 68° were obtained. A 20-g. portion recrystallized repeatedly from ethyl acetate melted at 68–68.5° and gave $[\alpha]^{25°}_{D} = +62.2°$ in chloroform.

Anal. Subs., 0.0940: CO_2, 0.2656; H_2O, 0.0983. Calcd. for $C_{18}H_{32}O_2$: C, 77.07; H, 11.51. Found: C, 77.07; H, 11.67.

Fusion of Chaulmoogric Acid with Resorcinol and Zinc Chloride.—Eleven grams of chaulmoogric acid, 3.9 g. of resorcinol and 4.9 g. of anhydrous zinc chloride were heated at 100–105° with constant stirring for one hour. Resorcinol and zinc chloride were removed and the residue distilled at 2 mm. pressure, but only 0.8 g. (6% yield) of very impure chaulmoogrylresorcinol was obtained. After several crystallizations from an ether–petroleum ether mixture a few tenths of a gram of material remained which melted at 68–71°. It was soluble in 10% sodium hydroxide solution, very soluble in ether, alcohol and acetone. When dissolved in alcohol a deep red color resulted upon the addition of a drop of ferric chloride solution.

Dihydrochaulmoogrylresorcinol was prepared from dihydrochaulmoogric acid by the preceding method except that the temperature and time of heating were identical with those used in the preparation of hexylresorcinol. This gave a 50% yield of the desired ketone and 20% of the acid was recovered. After several crystallizations from 95% acetone it melted at 89.5°.

---

[12] Shriner and Adams, THIS JOURNAL, 47, 2731 (1925).

This ketone was also prepared from dihydrochaulmoogryl chloride and resorcinol by application of a Friedel and Crafts reaction in nitrobenzene. A 70% yield was obtained, the product melting at 89.5" after repeated recrystallizations from acetone. Both ketone preparations gave the same oxime.

Anal. Subs., 0.0947: CO_2, 0.2665; H_2O, 0.0877. Calcd. for $C_{24}H_{38}O_3$: C, 76.94; H, 10.23. Found: C, 76.74; H, 10.36.

The oxime of dihydrochaulmoogrylresorcinol was prepared according to the method used by Hill and Evans.[13] Two grams of dihydrochaulmoogrylresorcinol and 0.5 g. of hydroxylamine hydrochloride were added to 8 cc. of anhydrous pyridine and the solution heated on the steam-bath for ten hours. The oxime was obtained as an oil which crystallized on cooling. After several recrystallizations from benzene, it melted at 169–170°. The crystals were in the form of silvery flakes that turned yellow on exposure to light.

Anal. Calcd. for $C_{24}H_{39}O_3N$: N, 3.60. Found (Kjeldahl): N, 3.57, 3.49.

Chaulmoogryl chloride[M] was prepared most satisfactorily by the action of an excess of phosphorus trichloride on chaulmoogric acid at room temperature for twenty-four to thirty hours. The excess of trichloride was removed by vacuum distillation, when the acid chloride was obtained as a colorless liquid that'could not be purified by distillation.

Phosphorus pentachloride and thionyl chloride partly decomposed chaulmoogric acid. The potassium salt of chaulmoogric acid and thionyl chloride can be used satisfactorily for preparing the acid chloride except for the difficulty of preparing the anhydrous potassium salt.

Dimethyl and Monomethyl Ethers of Chaulmoogrylresorcinol.—Chaulmoogryl chloride from 26.0 g. of chaulmoogric acid and 12.5 g. of dimethylresorcinol were dissolved in 50 cc. of carbon disulfide and slowly added in small portions to 35 g. of powdered aluminum chloride covered with 25 cc. of carbon disulfide. The reaction was completed within two hours and water was then added to decompose any addition products formed. After extraction with ether and drying, the solvent was removed and the reaction product distilled under 2–3 mm. pressure. At 230–238° (uncorr.) 8.4 g. of a clear brownish-yellow oil was obtained (23% yield). Traces of chaulmoogric acid were removed from this and upon redistillation a bright yellow oil was collected that partially solidified on standing. By fractional crystallization from acetone silky needles were first obtained melting at 56–58" and a second more soluble fraction also crystallizing in needles melting at 34–36°. The two products were finally obtained in pure form by recrystallization from alcohol and acetone and melted at 65 and 46°, respectively. The higher-melting compound was less soluble, gave a red color when dissolved in alcohol and treated with a drop of ferric chloride solution, and gave a positive Millon's reaction. It was insoluble in sodium hydroxide solution and slowly developed a reddish color when exposed to the air. It was identified as 1-chaulmoogryl-2-hydroxy-4-methoxybenzene.

Anal. 1.2967 g. made up to 50.1 cc. in chloroform at 25" gave a rotation of $0.722" in a 4-dcm. tube; $[\alpha]_D^{25°} = +6.98°$. Subs., 0.1770: CO_2, 0.5001; H_2O, 0.1640. Calcd. for $C_{25}H_{38}O_3$: C, 77.66; H, 9.91. Found: C, 77.07; H, 10.34.

The compound melting at 46° gave no red color with ferric chloride solution and after careful purification no positive test with Millon's reagent. It was insoluble in sodium hydroxide and did not develop a red color on exposure to the air. It was identified as the methylated compound 1-chaulmoogryl-2,4-dimethoxybenzene.

---

[13] Evans, Doctor of Philosophy "Dissertation," Yale University, 1926.

[14] Powers and Gornall, J. *Chem. Soc.*, 85, 855 (1904).

Anal. 1.2470 g. made up to 27 cc. in chloroform at 25° gave a rotation of +3.47° in a 4-dcm. tube; $[\alpha]_D^{25°} = +18.78°$. Subs., 0.1310, 0.1174: CO_2, 0.3715, 0.3355; H_2O, 0.1207, 0.1083. Calcd. for $C_{26}H_{40}O_3$: C, 77.94; H, 10.07; Found: C, 77.34, 77.93; H, 10.30, 10.38.

Mol. wt. (in ethylene bromide). Solvent, 38.86, 38.86, 38.86; solute, 0.1213, 0.3074, 0.4090; Δt, 0.094°, 0.239°, 0.315°. Calcd. for $C_{26}H_{40}O_3$: 400.3. Found: 398, 397, 401; average, 398.

When the above procedure was modified by keeping the reaction temperature at 30–35° and adding the aluminum chloride to the chaulmoogryl chloride and resorcinol dissolved in carbon disulfide, yields of 40% were obtained, dimethylchaulmoogrylresorcinol being the only product identified. When anhydrous ferric chloride was used as the catalyst no demethylation took place by either procedure but the yields were much lower.

Esters of Resorcinol.—The anhydrous monopotassium salt of resorcinol was prepared by a procedure similar to that used by De Forcrand in preparing the monosodium salt.[15] It was a light colored, hard mass and was quite hygroscopic.

Seventeen and eight-tenths grams of this potassium salt of resorcinol was suspended in 125 cc. of dry ether and chaulmoogryl chloride (from 25 g. of chaulmoogric acid) dissolved in 75 cc. of ether slowly added. Immediate reaction occurred with the separation of potassium chloride. After this was complete water was added, the ether layer separated, washed first with water and then with sodium carbonate until free from chaulmoogric acid. The solvent was then removed, the reaction product dissolved in petroleum ether and washed with water to remove any unaltered resorcinol; it was dried and finally distilled under 2–3 mm. pressure. At 238–240° (uncorr.) 2.8 g. of a light yellow oil distilled over which immediately solidified; then at 270–281° (uncorr.), 11.7 g. of an almost colorless oil was obtained which also solidified. When crystallized from petroleum ether glistening plates were obtained melting at 51°. The compound is very soluble in hot petroleum ether, ether or acetone, but difficultly soluble in alcohol. Analysis and molecular weight determinations indicated that we were dealing with **resorcinol dichaulmoograte.**

Anal. 0.6158 g. made up to 27 cc. by chloroform at 25° gave +4.19° in a 4-dcm. tube. $[\alpha]_D^{25°} = +45.93°$. Subs., 0.0747, 0.0948: CO_2, 0.2140, 0.2715; H_2O, 0.0703, 0.0857. Calcd. for $C_{42}H_{66}O_4$: C, 79.42; H, 10.47. Found: C, 78.13, 78.10; H, 10.53, 10.12.

Mol. wt. (in ethylene bromide). Solvent, 32.53, 32.53, 32.53; solute, 0.0815, 0.1420, 0.2406; Δt, 0.045°, 0.078°, 0.134°. Calcd. for $C_{42}H_{66}O_4$: 634.5. Found: 668, 672, 660; average, 667.

Chaulmoogrylresorcinol.—Chaulmoogryl chloride from 50 g. of chaulmoogric acid and 26 g. of resorcinol were dissolved in 150 cc. of anhydrous nitrobenzene. The temperature was maintained at 30–35° while 29 g. of aluminum chloride was added in small portions followed by shaking. After standing for a few minutes the mixture was cooled and cold dilute hydrochloric acid and cracked ice were added. Ether extraction was then applied and the ether solution dried over anhydrous sodium sulfate. After removing all ether and nitrobenzene by vacuum distillation, the remaining oil was distilled under 2–3 mm. pressure, when we obtained thirty-eight grams of a light yellow oil which, on cooling, crystallized in long needles. On crystallization from acetone it was obtained in the form of small colorless needles melting at 83°. Removal of the nitrobenzene by vacuum distillation was more satisfactory than by steam distillation.

Anal. 1.284 g. made up to 50.8 cc. in chloroform at 25° gave a rotation of +0.14°

---

[15] De Forcrand, *Ann. chim. phys.*, [6] 30, 67 (1893).

in a 4-dcm. tube. $[\alpha]_D^{25°} = +1.38$. Subs., 0.0810: CO_2, 0.2286; H_2O, 0.0728. Calcd. for $C_{24}H_{36}O_3$: C, 77.36; H, 9.74. Found: C, 76.96; H, 10.05.

The oxime of chaulmoogrylresorcinol was prepared by the method previously described. It melted at 152–154° and after three crystallizations from benzene melted sharply at 161°. In appearance it was indistinguishable from the oxime of dihydrochaulmoogrylresorcinol and, like it, turned yellow on exposure to light.

Anal. Optical activity practically within experimental error, \$0.02 °, in a 4-dcm. tube. Calcd. for $C_{24}H_{37}O_3N$: N, 3.61. Found (Kjeldahl): N, 3.54, 3.55.

1-Cyclopentenyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane.—Eight grains of chaulmoogrylresorcinol was reduced by the Clemmensen method, stirring constantly and keeping a small amount of an ether–benzene mixture returning to the reduction flask from a reflux condenser. When no solvent was allowed to reflux, the material soon formed a butter-like emulsion which completely prevented mixing by the stirrer. Only a few cubic centimeters of ether or ether–benzene mixture was needed to prevent emulsification. The ferric chloride test for unreduced ketone was negative after seven hours, though reduction was continued for one hour longer. The reduced material was dissolved in ether, washed with water and the solution dried over anhydrous sodium sulfate. After removal of the ether, the oil obtained was distilled under 2–3 mm. pressure. It distilled at 245–247° (uncorr.) as a colorless oil which immediately solidified on cooling. This was further purified by crystallization from a petroleum ether–ligroin mixture, separating as needles melting at 68°. It was very soluble in alcohol, acetone or ether and dissolved immediately in 10% sodium hydroxide solution. It was moderately soluble in chloroform, ligroin and petroleum ether.

Anal. 2.1038 g. made up to 27 cc. in chloroform at 25° showed very slight or no optical activity in a 4-dcm. tube. Subs., 0.1175, 0.1042, 0.0865: CO_2, 0.3458, 0.3061, 0.2551; H_2O, 0.1147, 0.1018, 0.0842. Calcd. for $C_{24}H_{38}O_2$: C, 80.38; H, 10.68. Found: C, 80.26, 80.11, 80.42; H, 10.92, 10.93, 10.89.

1-Cyclopentenyl-13-(2-hydroxy-4-methoxyphenyl)-*n*-tridecane.—Two and eight-tenths grams of the monomethyl ether of chaulmoogrylresorcinol (1-chaulmoogryl-2-hydroxy-4-methoxybenzene) was reduced by the Clemmensen method; reduction was complete in six hours. A practically pure product was obtained and after two crystallizations from petroleum ether it melted at 47.5°. It crystallized in the form of pearly flakes.

Anal. 0.3890 g. made up to 27.1 cc. with chloroform at 25° gave a rotation of +0.354° in a 4-dcm. tube; $[\alpha]_D^{25°} = +6.15°$. Subs., 0.1086: CO_2, 0.3204; H_2O, 0.1058. Calcd. for $C_{25}H_{40}O_2$: C, 80.58, H, 10.82. Found: C, 80.46; H, 10.90.

Mol. wt. (in ethylene bromide). Solvent, 33.08, 33.08; solute, 0.0730, 0.1472; At, 0.073°, 0.147°. Calcd. for $C_{25}H_{40}O_2$: 372.3. Found: 363, 364; average, 364.

1-Cyclopentenyl-13-(2,4-dimethoxyphenyl)-*n*-tridecane.—Fourteen and seven-tenths grams of the dimethyl ether of chaulmoogrylresorcinol melting at 40° and containing a trace of the mono-methyl ether, as indicated by the ferric chloride test, was reduced by the Clemmensen method. Since no color test could be used to show the presence of unreduced ketone, the reduction was continued for eighteen hours. After three distillations the reduced material was obtained as a practically colorless oil, boiling at 250–252" (uncorr.) under 2 mm. pressure. It failed to solidify when cooled in a freezing mixture; n^{28}, 1.5414; d_{25}^{25}, 0.955.

Optical Activity.—1.070 g. made up to 10 cc. in chloroform at 25° gave a rotation of +1.02°; $[\alpha]_D^{25°} = +9.53°$.

1-Cyclopentyl-13-(2,4-dihydroxyphenyl)-*n*-tridecane.—Two and three-tenths grams of dihydrochaulmoogrylresorcinol was reduced by the Clemmensen method. The reduction required about nine hours, as the ketone reduced much less readily than the other combinations containing the chaulmoogryl group. A light yellow product was obtained that crystallized from ligroin in hard crystalline masses melting at 73–74".

Anal. Subs., 0.0647: CO_2, 0.1886; H_2O, 0.0649. Calcd. for $C_{24}H_{40}O_3$: C, 79.93; H, 11.19. Found: C, 79.50, H, 11.23.

Bacteriological **Study**

Preliminary experiments with chaulmoogrylresorcinol indicate a very low toxicity when given by mouth to rabbits or intramuscularly to rats. Tested against B. *thyphosum* the compound exerts little bactericidal or antiseptic action. It seems not improbable that this compound and lower homologs may be bactericidal for the acid-fast organisms such as leprosy and tuberculosis bacillus, through the ability of the compound to dissolve in the fat complexes of these organisms, even though the substance appears to be inert against the typhoid bacillus. Its bactericidal study is now in progress and a clinical investigation will follow.

Summary

1. The preparation of chaulmoogrylresorcinol and some of its derivatives are described.
2. The ketones prepared have been shown to be easily reduced to the corresponding alkyl resorcinols by the action of zinc amalgam.
3. The cyclopentenyl group in chaulmoogric acid is not reduced by the action of zinc amalgam.
4. The investigation of lower members of this homologous series will be continued in the Sterling Laboratory.

NEW HAVEN, CONNECTICUT

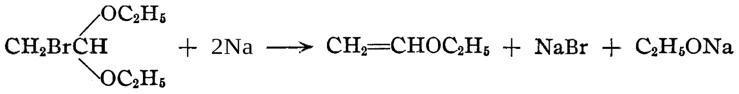
[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

THE ACTION OF METALLIC SODIUM ON BROMINATED CYCLIC ACETALS[1]

BY HAROLD S. HILL[2] AND G. J. C. POTTER

RECEIVED DECEMBER 6, 1928 PUBLISHED MAY 6, 1929

Wislicenus[3] showed that the reaction of bromo-ethylal with metallic sodium proceeded according to the following equation



$$CH_2BrCH\begin{matrix} \diagup OC_2H_5 \\ \\ \diagdown OC_2H_5 \end{matrix} + 2Na \longrightarrow CH_2{=}CHOC_2H_5 + NaBr + C_2H_5ONa \qquad (1)$$

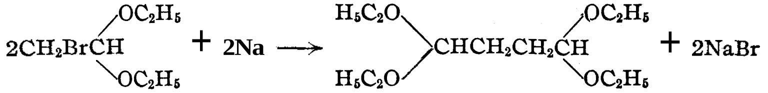
---

[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their appreciation of the facilities placed at their disposal by the three cooperating agencies.

[2] Research Fellow, Canadian Pulp and Paper Association.

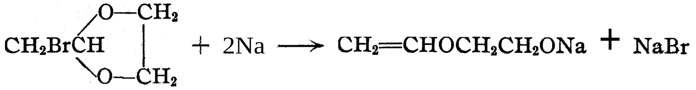
[3] Wislicenus, *Ann.*, 192, 106 (1878).

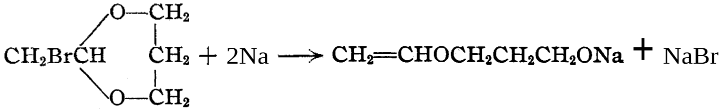
and that this unusual change took place to the exclusion of a Wurtz synthesis which might be expected to link up two molecules of the acetal


(2)

Quite recently the action of sodium on bromo-ethylidene ethylene glycol and bromo-ethylidene trimethylene glycol has been investigated.[4]

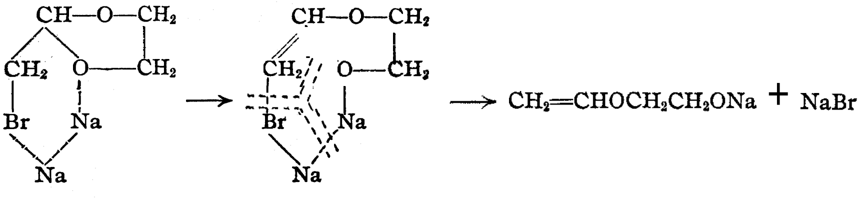
It has been found that these cyclic acetals in dry ether solution react smoothly at low temperatures with the metal and that a change similar to (1) takes place, yielding a vinyl derivative as the only product.


(3)

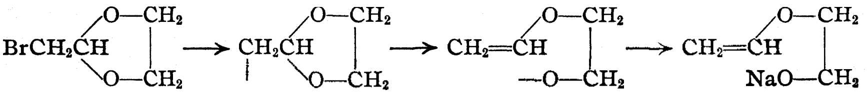

(4)

There are two obvious though nevertheless significant points regarding these reactions: (1) the absence of the usual Wurtz synthesis, as in (2); (2) the fact that the metal attacks the bromine and only one of the oxygen atoms. There may also be added the observations that: (3) without the oxygen in the molecule (substitution of O by CH_2, for example,) no unsaturation would have resulted; (4) without the bromine in the molecule no reaction at all would have resulted. (Ethylidene glycol may be refluxed over sodium without change.)

A conclusion may be drawn, therefore, that the above reactions are due to some combined influence of the bromine and oxygen atoms and that the role played by the one is dependent on that of the other. With these requirements in mind a mechanism scheme was proposed earlier[5] which embodied Erlenmeyer's theory of intermediate cyclization in chemical reaction as follows


(A)

An alternative series of changes may be


(B)

Hill and Pidgeon, This journal, 50, 2718, 2725 (1928).

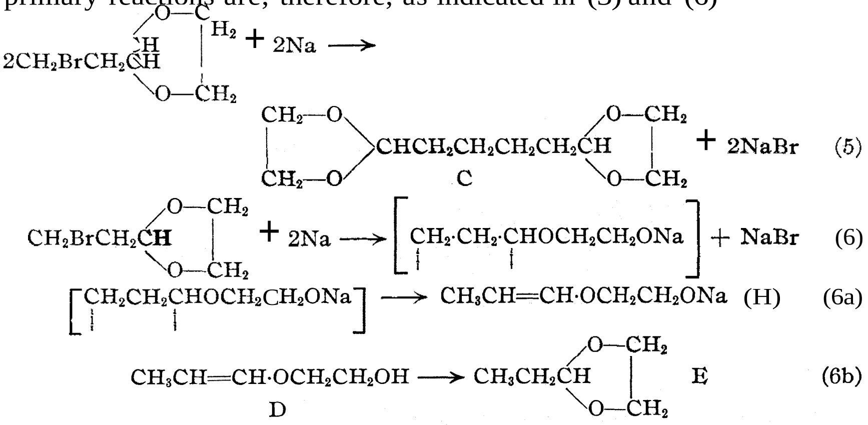
Hibbert and Hill, *ibid.*, 45, 740 (1923).

but in this scheme it is more difficultto account for the absence of a Wurtz synthesis.

In all of the above cases the bromine is on the α-carbon of the aldehyde residue. It seemed that similar reactions carried out with cyclic acetals having the halogen on the @-carbonmight throw further light on the nature of the changes taking place. Such information might also have a bearing on the question regarding the function of sodium as a polymerization catalyst.

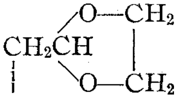
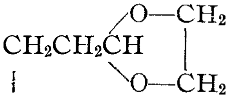
For this investigation β-bromopropylidene glycol and β-bromobutylidene glycol were synthesized by the reaction of acrolein and crotonaldehyde, respectively, with ethylene glycol in the presence of an excess of dry hydrogen bromide.

The Action of Sodium on **β-Bromopropylidene Glycol.**—β-Bromopropylidene glycol was found to react smoothly with metallic sodium in dry ether solution. The product instead of being exclusively a vinyl derivative as in the case of the a-bromo homolog proved to be a mixture of di-1,6-hexylidene glycol, C, hydroxy-ethyl-0-methylvinyl ether, D, and propylidene glycol, E, as well as smaller amounts of indefinite products. Propylidene glycol is presumably a secondary product resulting from a partial rearrangement (6b) of the vinyl derivative during distillation. The two primary reactions are, therefore, as indicated in (5) and (6)



The latter transformation (Gb) takes place very rapidly in the presence of a trace of 50% sulfuric acid although it does not have the explosive or quantitative nature of the similar rearrangement of hydroxyethylvinyl ether.[4] Other products besides E are noticeable and it is possible that the rearrangement is complicated by a partial reversal of the reaction indicated in (6a).

Reaction (6a) is of interest since it is an example of unsaturation shifting from one atom to another, a process which undoubtedly takes place in the intermediate stages of many organic reactions.

In (5) a Wurtz synthesis has taken place and from this it may be concluded that the interdependence of the halogen and oxygen atoms is much less marked in the reaction of sodium with a β-bromo- than with an α-bromoalkylidene glycol. If Mechanism A is accepted, this may be explained as due to a less tendency to form the necessary seven-membered cyclic intermediate. On the other hand, if Mechanism B should prove correct, it means that the radical  is less stable than  in the presence of sodium.

The structure of the diacetal, C, was established by its hydrolysis to hexyl dialdehyde which underwent intramolecular "crotonization" to give A-cyclopentene aldehyde as described by Read and Hibbert.[6] The cyclic aldehyde was not isolated in a pure state but was identified by its semicarbazone.

The Action of Sodium on β-Bromobutylidene Glycol.—β-Bromobutylidene glycol reacted with sodium in an analogous manner to its lower homolog, β-bromopropylidene glycol. The reaction took a mixed course, effecting a union of two acetal residues on the one hand and attacking both the bromine and one oxygen atom to give a vinyl derivative and its rearrangement product, butylidene glycol on the other. Here also much of the unsaturated product underwent cyclization during isolation.

Conclusions

The results of the above and earlier experiments indicate that the position of the halogen in brominated cyclic acetals has a marked influence on the course of their reactions with metallic sodium. If the bromine is on the α-carbon a vinyl derivative is formed almost exclusively. A bromine attached to a β-carbon, however, causes more complicated changes, for in addition to the latter reaction, a Wurtz synthesis takes place. A bromine on a y-carbon would presumably still further increase the tendency toward the linking up of two molecules.

Experimental Part

Preparation of β-Bromopropylidene Glycol.—One hundred and sixty g. (2.5 moles) of ethylene glycol was put in a 1-liter three-necked flask equipped with a mechanical stirrer operating through a mercury seal, a calcium chloride drying tube, a dropping funnel cooled by an ice-bath and containing 112 g. (2 moles) of pure acrolein, and a delivery tube. The latter was connected with a source of dry hydrogen bromide (prepared catalytically by passing a mixture of bromine and hydrogen over an electrically heated platinum spiral). The flask was cooled in an ice-bath and about 100 g. of dry hydrogen bromide was bubbled into the glycol with stirring. At this point acrolein was allowed to drop in slowly, continuing the passage of hydrogen bromide until about 100 g. more had been passed in (2.5 moles in all). After this and all of the acrolein had been

---

[6] Read and Hibbert, THIS JOURNAL, 46, 1281 (1924).

added, the mixture was stirred for two hours, allowed to stand overnight without further cooling, and then stirred for two hours more at room temperature. The mixture was extracted three times with ether and the latter solution neutralized with solid sodium bicarbonate, filtered, washed several times with small amounts of cold water arid dried over potassium carbonate. Fractionation under reduced pressure gave a small fore-run of sharp smelling products and 236 *g.* of β-bromopropylidene glycol, b. p. 72–73° (10 mm.); yield, 65% reckoned on the amount of acrolein used. There appeared to be a slight amount of decomposition during distillation and the final product possessed a somewhat sharp odor. There is less decomposition if no air is admitted through the capillary tube used to aid boiling.

Anal. Subs., 0.1539: AgBr, 0.1577. Calcd. for $C_5H_9O_2Br$: Br, 44.17. Found: Br, 43.61.

Preparation of **β-Bromobutylidene** Glycol.—This was prepared in an identical manner to β-bromopropylidene glycol, substituting crotonaldehyde for acrolein. From 124 g. (2 moles) of ethylene glycol, 200 g. (2.5 moles) of hydrogen bromide and 140 g. (2 moles) of crotonaldehyde, there was obtained from the first distillation 278 g. of β-bromobutylidene glycol, b. p. 70–78° (10 mm.). Refractionation gave 220 *g.*, b. p. 76–78" (10 mm.), or 56% of the theoretical yield reckoned on the amount of crotonaldehyde used.

Anal. Subs., 0.1683: AgBr, 0.1667. Calcd. for $C_6H_{11}O_2$: Br, 41.02. Found: Br, 42.15.

This product on long standing decomposed, giving off hydrogen bromide. A sample in a well stoppered, brown glass bottle had changed to a black, solid mass on standing for one year.

Action of Sodium on **β-Bromopropylidene** Glycol.—Fifty-four g. of β-bromopropylidene glycol was dissolved in 100 cc. of absolute ether in a three-necked flask equipped with a reflux condenser and an efficient mechanical stirrer protected from the atmosphere. Fourteen g. of freshly cut sodium was added and the mixture warmed to gentle boiling for sixteen hours with vigorous stirring. The reaction was slower than in the case of α-bromo acetals. The sludge of accumulated salts was flushed with ether through a wire gauze to filter out unchanged sodium amounting to 6 g. The difference in the reaction of α- and β-brominated acetals is noticeable at this point from the relative amount of sodium used up by each. The β-bromo derivative used up considerably less sodium, indicating that more of the reaction linking up two molecules had taken place. Enough water to dissolve the salts was added cautiously, the mixture extracted three times with ether and the ether extract dried over potassium carbonate. Preliminary fractionation separated the product roughly into four parts: (1) b. p. 104–109° (760 mm.), yield, 7 g. (it is better to take this fraction off at about 100 mm. pressure in order to avoid overheating subsequent fractions); (2) b. p. 60–63° (16 mm.), yield, 2 g.; (3) b. p. 144–150° (11 mm.), yield, 5 g.; (4) residue, yield, 5 g.

Fraction (1). Propylidene Glycol.—This when refractionated gave pure propylidene glycol, b. p. 106–107" (760 mm.).

And. Subs., 0.2090: CO_2, 0.4470; H_2O, 0.1792. Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80. Found: C, 58.44; H, 9.52.

This product was identical in every way with propylidene glycol prepared from propionaldehyde and ethylene glycol.

Fraction (2). **Hydroxyethyl-8-methylvinyl** Ether.—The combined yield of this product from several runs was refractionated, giving a product of b. p. 60–61° (16 mm.).

Anal. Subs., 0 2021: CO_2, 0.4365; H_2O, 0.1742. Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80. Found: C, 58.90; H, 9.61.

The product was unsaturated against bromine in carbon tetrachloride and gave test reactions for the hydroxyl group. With a trace of 50% sulfuric acid it underwent a rapid reaction, from the product of which propylidene glycol was isolated, b. p. 106° (760 mm.).

The relative yields of Fractions (1) and (2) varied in different preparations, thus further indicating that the former is a secondary rearrangement product of the latter.

Fraction (3). **Di-1,6-hexylidene** Glycol.—This product on refractionation gave a colorless, viscous oil, b. p. 139–140° (10 mm.), which crystallized on cooling in an ice-bath.

Anal. Subs., 0.2074: CO_2, 0.4480; H_2O, 0.1662. Calcd. for $C_{10}H_{18}O_4$: C, 59.40; H, 8.91. Found: C, 59.02; H, 8.90.

Identification of **Fraction (3)**.—Two g., b. p. 139–140° (10 mm.), was heated for two hours under reflux with 5 cc. of 5% phosphoric acid. The reaction mixture was extracted several times with ether and the latter solution neutralized with potassium carbonate and dried over the same salt. Distillation of the solvent left a small amount of an oil having the pungent aromatic odor described by Read and Hibbert for Δ-cyclopentene. The semicarbazone prepared in the usual manner gave m. p. 209° (corr.) (R. and H. give 208–209°).

Anal. Subs., 0.1529; CO_2, 0.3062; H_2O, 0.0972. Calcd. for $C_7H_{11}ON_3$: C, 54.90; H, 7.19. Found: C, 54.61; H, 7.06.

Action of Sodium on **β-Bromobutylidene** Glycol.—The reaction was carried out in the same manner as with β-bromopropylidene glycol, and here also fractionation of the product yielded three main fractions and a residue.

Fraction (1), butylidene glycol, b. p. 128–135° (760 mm.), yielded for the most part butylidene glycol, b. p. 132–133° (760 mm.).

Anal. Subs., 0.2024: CO_2, 0.4589; H_2O, 0.1827. Calcd. for $C_6H_{12}O_2$: C, 62.07; H, 10.30. Found: C, 61.88; H, 10.03.

Fraction (2), **hydroxyethyl-β-ethyl** vinyl ether, b. p. 60–65° (10 mm.). This product was unsaturated against bromine in carbon tetrachloride, gave positive tests for the hydroxyl group and underwent cyclization in the presence of a trace of 50% sulfuric acid, yielding butylidene glycol, b. p. 135°.

Anal. (Fraction (2)). Subs., 0.1990: CO_2, 0.4521; H_2O, 0.1790. Calcd. for $C_6H_{12}O_2$: C, 62.07; H, 10.30. Found: C, 61.96; H, 10.00.

Fraction (3), dimethyl-di-1,6-hexylidene glycol (?), b. p. 150–170° (15 mm.). It was impossible to obtain a sharp boiling product from this fraction but it is presumably an impure diacetal derivative corresponding to the di-1,6-hexylidene glycol isolated in the similar reaction with β-bromopropylidene glycol.

For the purpose of preparing these diacetal derivatives it would probably be more advantageous to extract them with dry ether from the original reaction mixture before the addition of water. This would effect their separation from hydroxyvinyl products, which would be left in the residue in the form of their sodium salts.

Summary

1. The synthesis of β-bromopropylidene glycol and β-bromobutylidene glycol has been carried out.

2. The reaction of these compounds with metallic sodium is described and compared with corresponding reactions of α-bromo acetals.

3. The mechanism of these reactions is discussed.

MONTREAL, QUEBEC, CANADA

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

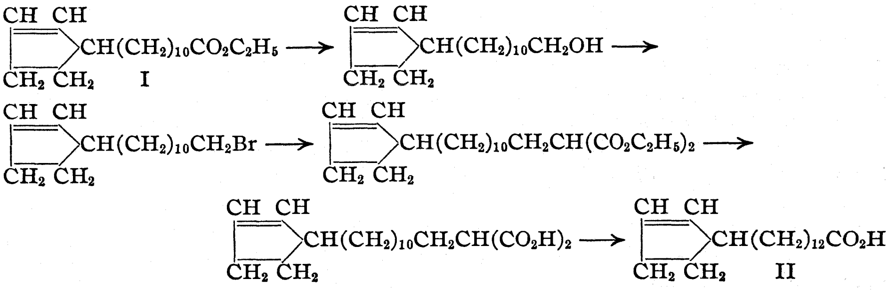
THE SYNTHESIS OF CHAULMOOGRIC ACID FROM HYDNOCARPIC ACID

By W. M. Stanley[1] and Roger Adams

Received December 7, 1928 Published May 6, 1929

In his early investigations on chaulmoogra oil and other oils of a similar character, Power[2] and his students isolated, in addition to chaulmoogric acid, hydnocarpic acid. This analyzed as a homolog of chaulmoogric acid. In order to confirm this conclusion, Power[3] oxidized hydnocarpic acid and isolated a di- and a tricarboxylic acid, the former of which proved to be n-decanedicarboxylic acid and the latter was assumed to be *n*-tridecane-α,α',γ-tricarboxylic acid. Since these oxidation products corresponded to those obtained from chaulmoogric acid, his conclusion was strengthened that the acids were homologs.

On account of the increasing importance of hydnocarpic acid and chaulmoogric acid, and on account of the fact that the correct structure for chaulmoogricacid, II, was found to be slightly different from that suggested by Power,[4] it seemed desirable to make further experiments to show the chemical relationship between these acids. This has been accomplished by conversion of hydnocarpic acid to chaulmoogric acid, II, through ethyl hydnocarpate, I, hydnocarpyl alcohol, hydnocarpyl bromide and hydnocarpylmalonic acid, successively.



No special comments need to be made concerning the well-known reactions involved. It should be stated, however, that the hydnocarpic acid used was not absolutely pure and consequently there was obtained in each step a certain amount of by-product which required careful fractionation for removal. No particular effort was made to purify completely each inter-

---

[1] This communication is a portion of a thesis submitted by W. M. Stanley in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Power and Barrowcliff, *J. Chem. Soc.*, 87, 884 (1905).

[3] Barrowcliff and Power, *ibid.*, 91, 557 (1907).

[4] Shriner and Adams, This journal, 47, 2727 (1925).

mediate step before conversion to the succeeding one, though each intermediate was purified for the determination of physical constants.

The hydnocarpylacetic acid obtained was contaminated with small amounts of other acids which were rather difficult to remove and required several fractional crystallizations. It was then possible to obtain a synthetic acid which had the same constants, melting point, rotation, etc., as the natural product (chaulmoogric acid). Moreover, the amides were compared and shown to be identical.

Perkins and Cruz[5] synthesized dl-chaulmoogric acid from simple organic compounds and showed that by oxidation the same decomposition products were obtained as from the natural, active form. The dl-form was not, however, resolved. Their investigation did not aid in the determination of the relationship of the natural hydnocarpic and chaulmoogric acids.

Experimental Part

Ethyl **Hydnocarpate.**—The hydnocarpic acid used in this investigation was kindly furnished by the Chemical Section of the Culion Leper Colony. The authors desire to express their appreciation for this material. The product had a melting point of 59.6" and a rotation of +69.4°.

A mixture of 250 g. of hydnocarpic acid, 400 g. of absolute ethyl alcohol and 7 g. of sulfuric acid was refluxed for two days. It was then cooled and poured into three times its volume of water containing 15 g. of sodium bicarbonate. The upper layer was separated and the slightly alkaline lower aqueous portion was extracted five times with ether and the ether extract washed twice with water. The ether extract was combined with the upper layer and again washed with water, dried over anhydrous magnesium sulfate, and distilled under diminished pressure. The yield was 246 g. (92%) of a product boiling at 160–165° (5 mm.) and having a rotation of +61.5° (0.5225 g. made up to 25 cc. in chloroform and used in a 1-dcm. tube). Twenty grams of hydnocarpic acid was recovered by acidifying the aqueous portion and extracting with ether. A 15-g. sample was fractionated and gave 9 g. of ethyl hydnocarpate, the physical constants of which did not change on further fractionation. The constants were: b. p., 143–144" (2 mm.); n^{25}_{D}, 1.4582; d^{25}_{4}, 0.9087; $[\alpha]_{\mathrm{D}}$, +70.5° (0.5186 g. made up to 25 cc. in chloroform and used in a 1-dcm. tube).

Power and Barrowcliff[2] report a boiling point of 211° (19 mm.) and a rotation of +51.6° on a 5-g. sample of ethyl hydnocarpate which they prepared. Sacks and Adams[6] report a boiling point of 217° (23 mm.) and n^{25}_{D}, 1.4577, on a 30-g. sample of ethyl hydnocarpate.

Hydnocarpyl Alcohol.—A total of 225 g. of ethyl hydnocarpate was reduced to hydnocarpyl alcohol in three separate reductions by the toluene method. In each experiment 75 g. of ethyl hydnocarpate, 500 cc. of absolute ethyl alcohol, 100 cc. of toluene and 70 g. of sodium were used.

A 5-liter, three-necked flask was fitted with a separatory funnel, a mechanical stirrer and an extra long condenser of large bore. In the flask were placed 70 g. of sodium and 100 cc. of toluene which had been dried over sodium, and the mixture was heated with a flame until the sodium melted. The stirrer was then started, the flame removed and the mixture allowed to cool until the molten sodium solidified into small

---

[5] Perkins and Cruz, THIS JOURNAL, 49, 1070 (1927).

[6] Sacks with Adams, *ibid.*, 48, 2395 (1926).

pellets. A mixture of 75 g. of ethyl hydnocarpate in 300 cc. of absolute ethyl alcohol was immediately run into the flask as rapidly as possible, followed immediately by 200 cc. of absolute ethyl alcohol. The stirring was continued and the mixture heated with a flame of sufficient size to keep the alcohol refluxing vigorously until practically all of the sodium had disappeared. The stirrer was stopped and the contents of the flask poured into an ordinary 5-liter flask. This was repeated twice and the three runs combined in the flask were heated on a steam-cone for ten hours. While still hot the mixture was washed with five times its volume of hot water or until the wash water was free of soap. It was washed once with water, then with water containing a small amount of sulfuric acid and finally with water. The wash water was combined and extracted four times with ether, the ether extract washed with water and then added to the main alcohol portion. The alkaline wash water was acidified and 25 g. of crude hydnocarpic acid was recovered. The solvent was removed and the alcohol distilled under diminished pressure. The yield was 90 g. (46%) of a product boiling at 170–175° (8 mm.) and having a rotation of +73.6° (0.7996 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube). Two high-boiling fractions consisting of 43 g. boiling at 185–210° (2 mm.) and 35 g. boiling above 210° (2 mm.) were obtained and probably consisted of dimolecular reduction products.

A 20-g. sample of the alcohol which was fractionated gave 15 g. of hydnocarpyl alcohol having the following constants: b. p., 144–145° (2 mm.); m. p., 23°; n_{D}^{25}, 1.4709; d_4^{25}, 0.8022; $[\alpha]_{\mathrm{D}}$, +75.2° (0.8592 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube). Further fractionation did not change these constants, although the high-boiling material from the first fractionation had a melting point of 27°, n_{D}^{27}, 1.4721, and $[\alpha]_{\mathrm{D}}$, +59.5. Sacks and Adams[6] report the following constants on a 12-g. sample of hydnocarpyl alcohol which was not subjected to further fractionation: b. p., 199.5° (14 mm.); m. p., 23°; n_{D}^{25}, 1.4733; $[\alpha]_{\mathrm{D}}$, +67.8° (0.8019 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube).

Hydnocarpyl Bromide.—A solution of 70 g. of hydnocarpyl alcohol in 150 cc. of dry toluene was placed in a 600-cc. flask fitted with a thermometer, calcium chloride tube and a separatory funnel, and cooled to 0° by means of an ice-bath. An ice-cooled solution of 65 g. of redistilled phosphorus tribromide in 70 cc. of dry toluene was then added sufficiently slowly so that the temperature of the reaction mixture did not rise above 5°. The reaction mixture was kept at 0° for six hours, then at room temperature for twelve hours and finally on a steam-cone for six hours. It was cooled and extracted with petroleum ether, the ether extract washed first with water and then with a solution of sodium carbonate, and finally dried for twelve hours over anhydrous potassium carbonate. The solvent was removed and the bromide was distilled under diminished pressure. The yield was 62 g. (70.5%) of a product boiling at 165–170° (5 mm.) and having a rotation of +19.4° (0.7521 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube). A 12-g. sample was fractionated to give 8 g. of hydnocarpyl bromide having the following constants: b. p., 156–157° (2 mm.); n_{D}^{25}, 1.4857; d_4^{25}, 1.0763; $[\alpha]_{\mathrm{D}}$, +27.4° (0.7604 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube). Further fractionation of the 8-g. sample did not cause any change in the constants. Sacks and Adams[6] report the following constants for hydnocarpyl bromide: b. p., 206–210° (14 mm.); m. p., 1°; n_{D}^{25}, 1.4871; $[\alpha]_{\mathrm{D}}$, +40.0° (0.5859 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube).

Monohydnocarpyl Diethyl Malonate.—The condensation of 50 g. of hydnocarpyl bromide with the sodium derivative of malonic ester was carried out in the usual way. The yield was 37 g. (59%) of a product having the following constants: b. p., 182–183° (2 mm.); n_{D}^{25}, 1.4601; d_4^{25}, 0.9519; $[\alpha]_{\mathrm{D}}$, $25.6" (0.6717 g. made up to 15 cc. in chloroform and used in a 1-dcm. tube).

Anal. Subs., 0.3200: CO_2, 0.8506; H_2O, 0.3018. Calcd. for $C_{23}H_{40}O_4$: C, 72.57; H, 10.60. Found: C, 72.49; H, 10.48.

Hydnocarpylacetic Acid (**Chaulmoogric** Acid).—Without isolating the intermediate malonic acid, 27 g. of monohydnocarpyl diethyl malonate was hydrolyzed to the malonic acid and then converted to the corresponding monobasic acid by the usual procedure.[7] The yield was 18 g. (92%) of a product boiling at 184–186° (1.4 mm.), melting at 61° and having a rotation of +38.3°. By careful fractional crystallizations from 80% ethyl alcohol (ethyl acetate and petroleum ether were used once each to remove any trace of ethyl chaulmoograte which might be formed), impurities of lower-melting products were eliminated and the least soluble chaulmoogric acid obtained which melted at 68° and had a rotation of +54.2°. Cold chloroform was added (about 10 cc. per g. of acid) until about two-thirds of the solid acid dissolved on shaking for two or three minutes. The insoluble portion was filtered and the product obtained by evaporation of the filtrate was recrystallized from 80% ethyl alcohol. After a second similar treatment with chloroform, the product obtained in the filtrate had a melting-point of 68° and a rotation of +61.9° which did not change on further treatment. A mixed melting point with pure natural chaulmoogric acid showed no depression.

Fractions obtained during the crystallization of the synthetic chaulmoogric acid had a melting point as low as 59° and a rotation as low as +19.5°. Apparently small amounts of impurities, presumably acids, were converted in each step in the process in a similar manner to the hydnocarpic acid and were not so easily removed from the final product as might have been expected.

Anal. Subs., 0.3162, 0.1200: CO_2, 0.8965; H_2O, 0.3196; 4.25 cc. of 0.1007 N alcoholic NaOH. Calcd. for $C_{18}H_{22}O_2$: C, 77.07; H, 11.51; neut. equiv., 280.26. Found: C, 77.32; H, 11.23; neut. equiv., 280.3.

Chaulmoogramide.—The amide of the synthetic chaulmoogric acid was made by the method described by Aschan[8a] and later by Power and Gornall[8b] and also by the method described by Shriner and Adams.[4] The melting point was 104° and a mixed melting point with chaulmoogramide made from natural chaulmoogric acid showed no depression.

Summary

Hydnocarpylacetic acid was prepared from hydnocarpic acid through hydnocarpyl ester, hydnocarpyl alcohol, hydnocarpyl bromide, hydnocarpylmalonic ester, and hydnocarpylmalonic acid. It proved to be identical with natural chaulmoogric acid.

URBANA, ILLINOIS

---

[7] Adams, Stanley and Stearns, THIS JOURNAL, 50, 1475 (1928).

[8] (a) Aschan, *Ber.*, 31, 2344 (1898); (b) Power and Gornall, *J. Chem. Soc.*, **85**, 855 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE COMPOSITION OF GUM ARABIC[1,2]

BY C. L. BUTLER AND LEONARD H. CRETCHER

RECEIVED DECEMBER 7, 1928 PUBLISHED MAY 6, 1929

Although a vast amount of research has been done in the field of carbohydrate chemistry, comparatively little attention has been given to the group of substances which may be classified under the heading of acid polysaccharides. In this group we find such substances as pectins, plant gums, hemicelluloses, mucilages, soluble specific substances produced by bacteria and alginic acid from algae. Most of these substances appear to be formed by modification of cellulose under the influence of enzymes, few, if any, of them being produced directly by photo-synthesis. Acid polysaccharides apparently play a very important, though poorly understood, role in natural processes. Any information that may be obtained regarding the structure of these substances should be of value in the elucidation of their functions in the immunology of infectious diseases and the physiology of plants. They are also of interest in connection with the problems of ropy bread, beer and wine. Among the members of this class of substances which we are investigating in this Laboratory are the plant gums.

Under the name of gums, a variety of substances have been described which differ considerably from one another both chemically and physiologically. The plant gums, as is well known, are salts of very complex organic acids usually with calcium, magnesium and potassium. These complex acids are built up of hexose, pentose and methylpentose units in combination with the acidic part of the molecule. The facts that many of them liberate carbon dioxide on heating with 12% hydrochloric acid[3] and that they give the naphtho-resorcin test[4] indicate that they contain uronic acid units.[5] In fact Anderson and his co-workers have reported the presence of glucuronic acid in mesquite gum and galacturonic acid in cholla gum.[6]

But little work has been done on the acidic nucleus of gums since the early researches of O'Sullivan. This author hydrolyzed arabic acid—

---

[1] Presented before the Organic Chemistry Division of the American Chemical Society at the Swampscott Meeting, September, 1928.

[2] Cf. Cretcher and Butler, *Science*, 68, 116 (1928), for a preliminary discussion on the nature of the acidic substance formed on the hydrolysis of this gum.

[3] (a) Nanji, Patton and Ling, *J. Soc. Chem. Ind*, 44, 253T (1925); (b) Anderson and Sands, THIS JOURNAL, 48, 3172 (1926).

[4] Tollens, Ber., 41, 1788 (1908).

[5] Widsoe and Tollens, *ibid.*, **33**, 132 (1900); see also ref. 1.

[6] Abstract of papers presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis Meeting, April, 1928.

from gum arabic—with dilute sulfuric acid and isolated a stable acid of lower molecular weight which he called X-arabinosic acid.[7] He assigned to the substance the formula $C_{23}H_{38}O_{22}$. Similarly O'Sullivan prepared so-called C_{23} acids from gum tragacanth and from gedda gum.[8] Robinson, in 1906, also claimed to have isolated a C_{23} acid from the gum of *Cochlospermum Gossypium*.[9] Various other gums have been investigated, but as stated above with little, if any, emphasis placed on the acidic nucleus.

A botanically authentic sample of Gum Arabic Cordofan from Acacia Senegal (L.) *Willd.* was hydrolyzed with 2% sulfuric acid and the acidic reaction product isolated by methods which are set forth in the experimental part of this paper. Analysis of the dried, purified salt indicated an aldobionic acid of formula $C_{12}H_{20}O_{12}$. This acid was analytically identical with the X-arabinosic acid of O'Sullivan,[10] who assigned to it the formula $C_{23}H_{38}O_{22}$ though his own analytical figures correspond as well to $C_{12}H_{20}O_{12}$. It gives a strong naphtho-resorcin test and reduces Fehling's solution. On boiling with 12% hydrochloric acid the correct amount of carbon dioxide is liberated, and the amount of iodine consumed in oxidation, as well as the percentage of calcium found, corresponds to the requirements of a compound of the formula given, containing one free aldehyde and one carboxyl group.

From a consideration of these facts the authors are led to wonder if the other C_{23} acids produced from gums and referred to in this paper are not in reality aldobionic acids. This point is being investigated.

The identity of the sugar constituent of this aldobionic acid was determined by hydrolysis with 5% sulfuric acid. This sugar had the correct rotation for d-galactose and formed mucic acid on oxidation. The acidic fraction was too small in amount to serve for purposes of identification due to the fact that, under the conditions of the hydrolysis, the uronic acid was largely destroyed. Simultaneous hydrolysis and oxidation of the aldobionic acid[11] was accomplished by boiling with hydrobromic acid in the presence of bromine. This led to the formation of saccharic acid, as shown by the isolation of acid potassium saccharate. The aldobionic acid is, therefore, galactoso-glucuronic. It is isomeric with the aldobionic acids isolated by Heidelberger and Goebel[11] from the polysaccharides produced by Pneumococcus Types II and III and from Friedlander Bacillus Types A, B and C.

In order to throw further light on the structure of this aldobionic acid, it was oxidized by the method of Goebel[12] to the dibasic acid, glucurono-

---

[7] O'Sullivan, J. *Chem. Soc.*, **45**, 41 (1884).

[8] O'Sullivan, *ibid.*, **59**, 1029 (1891); *ibid.*, **79**, 1164 (1901).

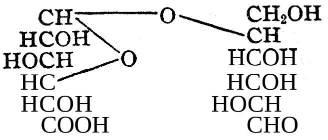
[9] Robinson, ibid., 89, 1496 (1906).

[10] Ref. 7, p. 45.

[11] Heidelberger and Goebel, J. *Biol. Chem.*, **74**, 613 (1927); *ibid.*, **74**, 619 (1927).

[12] Goebel, *ibid.*, **72**, 809 (1927).

galactonic. This substance was isolated and analyzed as the calcium salt. It gave a strong naphtho-resorcin test and on boiling with 12% hydrochloric acid liberated one molecular proportion of carbon dioxide. It did not reduce Fehling's solution. It is thus apparent that the uronic acid residue is intact in the oxidized acid and that the linkage between the two residues in the aldobionic acid is between the aldehyde of the glucuronic acid and a hydroxyl group of the galactose. Nothing, of course, is known as to which of the galactose hydroxyl groups enters into the glucosidic linking. The following formula is, therefore, purely hypothetical.



An interesting fact about this aldobionic acid is that, unless gum arabic is of bacterial origin, it is the first compound of this sort to have been found except in products of bacterial metabolism. It has been affirmed[13] and denied[14] that gums are of bacterial origin. Our results are interesting in this connection, though we do not offer them in evidence one way or the other.

Heidelberger, Avery and Goebel[15] have reported that occasional samples of gum arabic possess specific activity which they were able to enhance greatly by hydrolyzing until about 50% of the pentose contained in the gum was removed. The same authors have obtained an acid hydrolysis product of this gum which on analysis gave figures indicating that it was a somewhat impure aldobionic acid.[16] Since these investigators have shown that aldobionic acids are components of other specific carbohydrates,[11] the occurrence of this type of substance among the hydrolysis products of gum arabic does not seem surprising.

It has long been known that d-galactose and l-arabinose are formed on hydrolysis of this gum, or of arabic acid prepared from it.[17] Votoček and Vondraček[17c] have also reported the presence of d-glucose in the gum. Although the work done by us on the sugar fraction of the gum arabic hydrolysis product is not complete, the presence of d-galactose and l-arabinose has been confirmed, and the presence of the methylpentose,

---

[13] Smith, *Zentr. fur* Bakt., Abt. II, 10, 61 (1903); *ibid.*, 11, 698 (1904); *ibid.*, 15, 380, 796 (1906); J. *Soc. Chem. Ind.*, 23, 972 (1904); Prillieux and Delacroix, *Compt. rend.*, 118, 1430 (1894); Aderhold, *Arbt. biol. Abt. Gesundheitsamt.*, 2, 515 (1912).

[14] Rathay, *Zentr. fur Bakt.*, Abt. II, 2, 620 (1896); Sorauer, Z. *Pflanzenkrankh. Pflanzenschutz*, 25, 71 (1915).

[15] Paper read before the Annual Meeting of the American Chemical Society, Philadelphia, September, 1926.

[16] Private communication.

[17] (a) Kiliani, *Ber.*, 13,2304 (1880); (b) *ibid.*, 15, 34 (1882); (c) Votoček and Vondraček, *ibid.*, 37, 3858 (1904).

rhamnose, has been established. We prepared arabic acid (the ash-free gum) according to the method of Neubauer,[18] and analyzed it for pentose and methylpentose by the furfural-phloroglucid method;[19] for galactose by oxidation and isolation of mucic acid:[20] for uronic acid carbon dioxide by the Lefevre method;[21] and for carbon and hydrogen. The results are shown in Table I. The figures correspond roughly to 1 molecule of aldobionic acid, 2 of galactose, 3 of arabinose and 1 of methylpentose.

TABLE I

RESULTS OF ANALYSES

Galactoso-glucuronic acid	28.3%
Hexose (as galactose)	29.5%
Pentose (as arabinose)	34.4%
Methylpentose (as rhamnose hydrate)	14.2%
Total	106.4%

Titration of the acid with sodium hydroxide solution gave an equivalent weight of 1030. Titration with alkali in hot and cold solution also showed that arabic acid exists to the extent of about 22% as lactone.

Experimental Part

Hydrolysis of Gum Arabic by Dilute Sulfuric Acid.—Five hundred grams of gum arabic, $[\alpha]^{25}_{D} = -34.05°$ (dry basis), containing 2.72% of ash and 9.89% of moisture was dissolved in one and one-half liters of water and to this solution was added a solution of 64 g. of sulfuric acid in a liter of water. The solution thus prepared contained arabic acid dissolved in 2% sulfuric acid. It was refluxed gently and the course of the hydrolysis was followed by polarimetric readings. When the observed rotation ($l = 1$) reached +9.4°, further heating caused but slight increase in rotation and the hydrolysis was considered to be complete. This required about twenty hours.

Isolation of Calcium Aldobionate.—An excess of calcium carbonate was then added, the mixture warmed for several hours on a water-bath and allowed to stand overnight. It was filtered and the precipitate washed with a little water. After two treatments with "Nuchar" a clear, pale yellow liquid was obtained. This was evaporated *in vacuo* to a sirup and a crude separation into acidic and non-acidic parts was made by addition of ethyl alcohol. Some colored impurities were separated by fractional precipitation from water with ethyl alcohol.[11]

Final purification was accomplished by several precipitations from a concentrated water solution by pouring with stirring into about 10 volumes of methyl alcohol. The yield of calcium salt was 44 g. An additional 10 g. of salt was obtained from the methyl alcoholic mother liquors (see page 1524) making the total yield 54 g.

This salt was quite soluble in water. A sample of 1.25 g. dissolved in water and made up to 25 cc. had an observed rotation of +0.18° in a 2-decimeter tube; $[\alpha]^{25}_{D} = +1.8°$. It reduced Fehling's solution and gave a strong naphtho-resorcin test.[22]

---

[18] Neubauer, *Ann.*, 102, 105 (1857).

[19] Van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydesauren," Gebrüder Borntraeger, Berlin, 1920, p. 63.

[20] Ref. 19, p. 123.

[21] Ref. 19, p. 71.

[22] Ref. 2; ref. 19, p. 55.

Anal. Subs., 0.2437: CO_2, by Lefevre method, 0.0282. 0.2388 required 12.7 cc. of $N/10$ iodine for oxidation.[12,23] Subs., 0.1316: CO_2, 0.1830; H_2O, 0.0636. Subs., 0.9549: $CaSO_4$, 0.1872. Calcd. for $(C_{12}H_{19}O_{12})_2Ca$: CO_2, 11.7; $N/10$ iodine, 12.7 cc.; C, 38.33; H, 5.07; Ca, 5.33. Found: CO_2, 11.6; C, 37.91; H, 5.36; Ca, 5.76.

The alcoholic sugar solution resulting from the separation and purification of the calcium salt was saved for further investigation.

Free Aldobionic Acid.—Several attempts to prepare the free aldobionic acid were made. However, this acid has a strong tendency toward lactone formation. On evaporation of the solution obtained after removal of calcium from the salt by means of oxalic acid, a mixture of lactone and acid was obtained. This mixture—a white powder—was soluble in water and methyl alcohol.

On titrating 0.2000 g. with sodium hydroxide in the cold in the presence of phenolphthalein, 4.5 cc. of $0.1N$ sodium hydroxide was required. On warming the solution an additional 1.2 cc. of alkali was neutralized. These figures correspond to an equilibrium mixture of 79.5% of acid and 20.5% of lactone. The theoretical total titration for such a mixture is 5.6 cc. of $0.1N$ alkali.

Anal. Subs., 0.1411: CO_2, 0.2123; H_2O, 0.0730. Calcd. for 79.5% of $C_{12}H_{20}O_{12}$ and 20.5% of $C_{12}H_{18}O_{11}$: C, 40.95; H, 5.60. Found: C, 41.05; H, 5.78.

A 1.00-g, sample of calcium aldobionate dissolved in water, acidified with twice the calculated amount of hydrochloric acid and made up to 25 cc. had an initial observed rotation of $+0.19°$ in a 2-decimeter tube; $[\alpha]^{25}_{D} = +2.5°$ (calculated on the basis of free acid liberated). After seventeen hours the rotation was $[\alpha]^{25}_{D} = +1.71°$.

The Components of the Aldobionic Acid

The Identification of the Sugar.—The calcium was removed from about 1.0 g. of calcium aldobionate by the calculated amount of oxalic acid and the solution of free aldobionic acid was evaporated to dryness in *vacuo.* Fifty cubic centimeters of 1.0 N sulfuric acid was then added and the solution was refluxed gently for eighteen hours. The hydrolysis product was boiled with an excess of barium carbonate and after cooling was filtered. The filtrate was evaporated to dryness *in vacuo* and the residue extracted with alcohol, thus separating a small amount of alcohol-insoluble barium salt from the sugar formed on hydrolysis of the aldobionic acid. The alcoholic solution of the sugar was treated with a little Nuchar and evaporated to dryness. The observed rotation for $C = 0.6$ and $l = 2$ was $+0.94°$; $[\alpha]^{25}_{D} = +78.3°$; $[\alpha]_D$ (galactose) $= +80°$.

The sugar was submitted to oxidation with nitric acid. After cooling the reaction mixture and scratching the dish, fine crystals of mucic acid separated. The reaction mixture was allowed to stand overnight; the mucic acid was then filtered off, washed several times with saturated mucic acid solution and once with water and dried; m. p. 219–220° (corr.).

The Identification of the Acid Part of the Molecule.—The barium salt resulting from the hydrolysis above described was so crude and so small in amount that identification was impossible. A sample of aldobionic acid, prepared by decomposing 2.17 g. of the calcium salt with the calculated amount of oxalic acid, was, therefore, submitted to simultaneous hydrolysis and oxidation according to the method of Heidelberger and Goebel.[11] That mucic acid was not formed was shown by the fact that no insoluble dibasic acid separated out of the reaction mixture even after seeding with a few crystals of pure mucic acid. After neutralizing the concentrated solution with 50% potassium hydroxide solution, it was acidified with glacial acetic acid. After standing for several days in an ice box, 0.25 g. of crude acid potassium saccharate separated from solution. The material was recrystallized from 1.0 cc. of water, dried and analyzed,

---

[23] Willstätter and Schudel, Ber., 51, 780 (1918).

Anal. Subs., 0.1148: K_2SO_4, 0.0410. Calcd. for $COOH(CHOH)_4COOK$: K, 15.75. Found: K, 16.02.

The Stability of Galactoso-glucuronic Acid in 1 N Sulfuric Acid.—The very small amount of barium salt obtained by hydrolyzing galactoso-glucuronic acid with 1.0 N sulfuric acid indicated considerable decomposition of the aldobionic acid by the hot dilute sulfuric acid. An estimation of the extent to which this decomposition took place was obtained by weighing the carbon dioxide evolved during hydrolysis. A solution of 1.0 g. of calcium aldobionate in 50 cc. of 1.0 N sulfuric acid was refluxed gently for eighteen and one-half hours in the Lefevre carbon dioxide apparatus. The carbon dioxide evolved weighed 0.0520 g. Thus the aldobionate was decomposed to the extent of about 44%, since complete removal of carboxyl would yield 0.1173 g. of carbon dioxide.

Oxidation of the Aldobionic Acid to a Dibasic Acid.—A sample of galactoso-glucuronic acid was oxidized with barium hypo-iodite according to the method of Goebel.[12] Two grams of calcium aldobionate yielded about 1.5 g. of reprecipitated calcium glucurono-galactonate.

Anal. Subs., 0.5000: $CaSO_4$, 0.1681. Subs., 0.4000: CO_2, 0.0429 (Lefevre method). Calcd. for $C_{10}H_{18}O_9(COO)_2Ca$: Ca, 9.75; CO_2, 10.73. Found: Ca, 9.88; CO_2, 10.72.

Analysis of Arabic Acid.—This substance was prepared from gum arabic according to the method of Neubauer.[13] A sample of 0.9490 g. (dry basis) of acid containing 5.1% moisture made up to 25 cc. in water had an observed rotation of −1.23° in a 1-decimeter tube; $[\alpha]_D^{25} = -32\ 36°$.

Anal. Subs. (dry), 0.1235: CO_2, 0.1978; H_2O, 0.0680. Found: C, 43.67; H, 6.15. Subs. (dry), 1.000: CO_2 (Lefevre method), 0.0353. Found: 3.53% of CO_2, equivalent to 14.1% of uronic acid anhydride. Subs. (containing 5 1% of moisture), 1.0537 (1.000 dry subs) required 7.6 cc. of $N/10$ NaOH for neutralization at room temperature using phenolphthalein, and 9.7 cc. when titrated to a permanent end-point in hot solution. Equivalent weight based on hot titration, 1030. Subs., 0.2372: 0.0146 g. of alcohol-soluble phloroglucid and 0.0799 g. of alcohol-insoluble phloroglucid. From the latter figure was deducted 0.0112 g. to allow for the phloroglucid due to the uronic acid.[24] Found: methylpentose (as rhamnose hydrate), 14.2; pentose (as arabinose), 34.4. Subs., 0 9100, 0.9100: mucic acid, 0.2870, 0.2795.[25] Found: galactose, 42.9, 41.8, average, 42.4.

Preliminary Work on the Identification of the Sugars Formed on Hydrolysis of Gum Arabic

Galactose.—The presence of this sugar was shown both by analysis of arabic acid by the mucic acid method[24] and by isolation of the sugar. The methyl alcoholic mother liquors from the purification of the crude calcium aldobionate were concentrated to 100 cc. and poured into 350 cc. of methyl alcohol. An equal volume of ethyl alcohol was added and the mixture was allowed to stand to permit the precipitate to settle. An additional 10 g. of calcium salt was thus obtained.

The mother liquor from this precipitation was evaporated to about 75 cc.; it gave no further precipitate with methyl alcohol. The liquor was poured with stirring into 500 cc. of ethyl alcohol and a sirupy layer separated out. This became granular on grinding with absolute ethyl alcohol. The material, vacuum dried at 80°, was found to contain 1.07% of calcium, corresponding to 20.06% of calcium aldobionate. A

---

[24] Ref. 19, p. 75.

[25] Ref. 19, p. 123

sample of 0.8762 g. made up to 25 cc. in water had an observed rotation of +4.33° in a 2-decimeter tube. If the small rotation of the aldobionate be neglected and allowance be made for 20% of (practically) inactive calcium salt, c = 2 8; $[\alpha]_D^{25}$ = +77.4°; for galactose $[\alpha]_D$ = +80°. On oxidation with nitric acid, mucic acid melting at 220° (corr.) was obtained. The substance was therefore impure galactose.

Arabinose and **Rhamnose.**—Practically pure arabinose of melting point 155–156° was isolated by the method of Anderson and Sands.[3] A sample of 1.00 g. made up to 25 cc. in water had an observed rotation of +8.16° in a 2-decimeter tube; $[\alpha]_D^{25}$ = +102°.

The presence of both *l*-arabinose and rhamnose was demonstrated in the main bulk of mother liquor from the separation of crude calcium aldobionate after removal of two crops of crystals consisting of a mixture of pentose (probably arabinose) and hexose (probably galactose). A sample of the sirup was evaporated to dryness and treated with diphenylhydrazine according to Van der Haar.[26] A diphenylhydrazone separated, which after several recrystallizations melted at 210–202° (corr.), Van der Haar gives 204° as the melting point of pure arabinose diphenylhydrazone.[27]

A second sample of sirup was evaporated to dryness *in vacuo* and treated with *p*-bromophenylhydrazine, also according to Van der Haar.[28] A bright yellow *p*-bromophenylosazone was thus obtained which melted, after repeated washings with 90% ethyl alcohol and acetone, at 217–218°. The substance did not depress the melting point of a sample of pure rhamnose p-bromophenylosazone prepared from rhamnose which also melted at 217–218°. The observed rotation for c = 2.47 in a 20–80 pyridine–alcohol mixture and l = 1, was +1.0°; $[\alpha]_D^{25}$ = +40.5°. The value found for rhamnose p-bromophenylosazone made from rhamnose was $[\alpha]_D^{25}$ = +0.95 where 1 = 1 and c = 2.34; $[\alpha]_D^{25}$ = +40.6°.

Anal. Subs., 0.2000: AgBr, 0.1510 by Stepanow's method. Calcd. for $C_{18}H_{20}O_3N_4Br_2$: Br, 31.96. Found: Br, 32.13.

Summary

1. Gum arabic and arabic acid prepared from this gum have been studied analytically and polarimetrically.
2. Rhamnose, d-galactose and *l*-arabinose have been identified in the sugar fraction of the hydrolysis product.
3. The acidic nucleus of the gum has been shown to be an aldobionic acid whose components are d-galactose and d-glucuronic acid.

PITTSBURGH, PENNSYLVANIA

---

[26] Ref. 19, p. 249.

[27] Ref. 19, p. 178.

[28] Ref. 19, pp. 217, 262.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A STUDY OF THE GERMICIDAL ACTIVITY OF DIARYL-SULFIDE PHENOLS

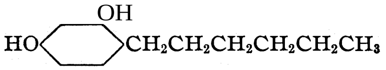
BY GUIDO E. HILBERT[1] AND TREAT B. JOHNSON

RECEIVED DECEMBER 11, 1928 PUBLISHED MAY 6, 1929

Introduction

The clinical success of hexylresorcinol, I, as a specific, internal antiseptic[2] was an incentive to extend our researches on germicides still further into the field of aromatic phenols. While various organic radicals have been incorporated into resorcinol with the object of increasing the phenol coefficient, no product has thus far been prepared in this series which has exhibited a higher germicidal value[3] than the hexyl compound. It is not to be assumed, however, that this hexyl combination represents the maximum in antiseptic efficiency that may be expected among organic constructions containing phenolic groups, and it was with the object of increasing this therapeutic or clinical value that we decided to extend our field of investigation along entirely new lines.

I



We have, therefore, inaugurated in this Laboratory a series of researches dealing with the question of the influence of sulfur linkages in organic combinations on germicidal activity. The study of the antiseptic properties of phenolic sulfur combinations has hitherto received little attention. The growing interest in the biochemistry of organic sulfur groupings[4] has stimulated a desire to acquire a better understanding of the influence of this element on antiseptic properties. The recent important work on

---

[1] Constructed from a dissertation presented by Guido Edward Hilbert in June, 1928, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. An abstract of this paper was presented at the Annual Meeting of the American Chemical Society held at Swampscott, Massachusetts, from September 10 to 15, 1928.

[2] Johnson and Hodge, THIS JOURNAL, 35, 1014 (1913); Johnson and Lane, *ibid.*, 43, 348 (1921); Leonard, *J. Am. Med. Assocn.*, 83, 2005 (1924); Dohme, Cox and Miller, THIS JOURNAL, 48, 1688 (1926); Leonard, *J. Urol.*, 12, 585 (1924); Leonard and Wood, *J. Am. Med. Assocn.*, 85, 1855 (1925); Henline, *J. Urol.*, 14, 119 (1925); Scott and Leonard, *Am. J. Dis. Children*, 31, 241 (1926); Wynne, *Minn. Med.*, April, 156 (1926); Brown, *J. Am. Med. Assocn.*, 86, 668 (1926); Leonard and Frobishers, *J. Urol.*, 15, 1 (1926); *Trans. Am. Assocn. Gen. Urol. Surg.*, 18, 333 (1925); Leonard and Feirer, *Dental Cosmos*, 3, 559 (1927); Damon, *Am. J. Public Health*, *17*, 279 (1927); Feirer and Leonard, *J. Am. Dent. Assocn.*, 1–17 (1927); *Dental Cosmos*, September, 1–12 (1927); "New and Non-Official Remedies," American Medical Association Council on Chemistry and Pharmacy, 1928, p. 336.

[3] Bartlett and Garland, THIS JOURNAL, 49, 2098 (1927); Talbot and Adams, *ibid.*, 49, 2040 (1927); Twiss, *ibid.*, 48, 2206 (1926); Klarmann, *ibid.*, 48, 2359 (1926).

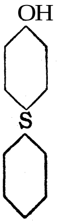
[4] Glutathione, ergothioneine, insulin, cystine, taurine, etc.

thyroxine[6] has clearly revealed the significance of the biological effect of incorporating an aromatic ether linkage into di-iodotyrosine[6] and the accepted conclusion regarding the constitution of thyroxine suggests that one might expect sulfur in aromatic sulfide combination to have an important and perhaps a favorable effect on the therapeutic action of phenols. A review of the literature reveals the fact that practically no attention has hitherto been paid to this clinical feature. Furthermore, our knowledge of the chemistry of aryl-sulfide phenols and their derivatives is very limited. New methods of synthesis must be worked up before the development of this field biologically can be advanced.[7]

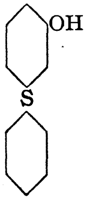
Aryl-Sulfide Phenols

The feature of our research to which we desire to direct special attention in this paper is the high phenol coefficient of the sulfide-phenol represented by Formula II, and the influence on germicidal activity by changing the structural position of the phenolic hydroxyl group in diphenyl sulfide. The degree of germicidal activity of the three isomers II, III and IV,

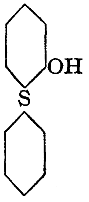
II



III



IV



is expressed in the order para>meta>ortho. An account of the preliminary bacteriological and toxicity tests, thus far conducted, is given in the Experimental Part of this paper.

Of the three isomeric phenols represented by Formulas II, III and IV, the para- and ortho-compounds have been previously reported in the literature. The para-compound was first obtained by Hinsberg[8] by allowing phenol to interact with benzenesulfinic acid. He was unsuccessful, however, in his attempts to purify the phenol and described it

$$2C_6H_5SO_2H \longrightarrow C_6H_5SO_2OH + C_6H_5SOH$$
$$C_6H_5SOH + C_6H_5OH = C_6H_5SC_6H_4OH + H_2O$$

as an undistillable oil; he presented no experimental evidence in support of its constitution. Its formation has since been reported by different

---

[5] C. R. Harington, *Biochem. J.*, 20, 293, 300 (1926). Harington and Barger, *ibid.*, 21, 169 (1927).

[6] Wheeler and Jamieson, *Am. Chem. J.*, 33, 365 (1905).

[7] Two new researches in this field are already in progress in the Sterling Laboratory and are being carried on in cooperation with Messrs. Shailer Bass and George H. Law (T. B. J.).

[8] Hinsberg, *Ber.*, 36, 107 (1903); German Patent 147,634; *Chem. Zentr.*, 75, 130 (1904).

investigators,[9] but in no single case have the properties of this phenol been correctly recorded, or has the constitution of Hinsberg's phenol been established. We have repeated Hinsberg's work and have succeeded in obtaining by dealkylation of the methyl ether of this phenol the pure sulfide-phenol, II, and established conclusively its constitution. This was accomplished by heating the methyl ether of the phenol, or the phenol II, with hydrobromic acid in acetic acid under pressure. The sulfide is thereby destroyed with formation of *p*-bromophenol and diphenyldisulfide as is expressed below. This behavior on prolonged heating with strong hydrobromic acid clears up the observation made by Hinsberg that

$$CH_3OC_6H_4SC_6H_5 + HBr = HOC_6H_4SC_6H_5 + CH_3Br$$
$$HOC_6H_4SC_6H_5 + HBr = HOC_6H_4Br + C_6H_5SH$$
$$2C_6H_5SH + O = C_6H_5S_2C_6H_5 + H_2O$$

p-methoxydiphenylsulfide yields methyl iodide and diphenyldisulfide when heated with hydriodic acid.

We have also established the constitution of Hinsberg's phenol by a new synthesis of the compound according to the method described by Lecher,[9c] who investigated the action of phenyl sulfochloride on Grignard reagents. This chloride was found to interact smoothly with *p*-bromoanisolemagnesium, yielding p-methoxydiphenylsulfide. On demethylating by heating with hydrobromic acid we obtained the same phenol as was formed in the Hinsberg process. Lecher showed also that the sulfide phenol, II, is formed in small yield by direct interaction of phenol with phenyl sulfochloride, but he did not succeed in purifying the compound thus obtained and the method of synthesis is of no practical value.

For the preparation of our three phenols we have made use of the Ziegler reaction. This investigator[10] showed that thiophenols do not interact with diazonium salts in a manner similar to phenols, but combine to give diazothio-ethers which break down at 70° giving an aromatic sulfide and nitrogen. If the reaction is run below 70" the sudden decomposition of an accumulation of the diazothio-ether may result in a violent explosion. The Ziegler reaction is one

$$C_6H_5SNa + C_6H_5N_2Cl = C_6H_5SC_6H_5 + NaCl + N_2$$

that is possible of wide application, but has not been utilized for the preparation of sulfide-phenol combinations. The reaction has been used by Graebe and Schultess,[11] Weedon and Doughty[12] and Mayer,[13] who applied it successfully with anthranilic acid, thereby leading to the later

---

[9] (a) Knoevenagel and Polack, *Ber.*, 41, 3331 (1908); (b) Bourgeois, *Rec. trav. chim.*, **31**, 32 (1912); (c) Lecher, *Ber.*, 58,413 (1925).

[10] Ziegler, *Ber.*, 23,2469 (1890).

[11] Graebe and Schultess, *Ann.*, 263, 1 (1891).

[12] Weedon and Doughty, *Am. Chem. J.*, 33,386 (1903).

[13] Mayer, *Ber.*, 42,3046 (1909).

development of the chemistry of phenylthiosalicylic acid and the thioxanthones. Mauthner,[14] however, reports no success in his attempts to apply the Ziegler reaction. We likewise have had no success in applying the Ziegler reaction with diazotized aminophenols. However, by treating thiophenol with the diazotized anisidines it is possible to obtain the methoxydiphenyl sulfides in good yields. For the practical application of the Ziegler reaction, two experimental conditions are essential: (1) that the interaction between diazonium salt and thiophenol take place at a temperature at which the former is stable, and thus prevent the formation of a phenol; (2) that the diazonium salt be soluble in water. If the diazonium salt is unstable at 70°, the reaction is best carried out at a lower temperature in the presence of copper powder, which was found to catalyze the decomposition of the diazothio-ether, thus avoiding a possible explosion.

In our study of this reaction we observed that a diazothio-ether can break down with formation of a sulfide and nitrogen and also with production of a diphenyldisulfide and nitrogen. The mechanism of this second change is not correctly understood. For a successful application of the Ziegler reaction it is necessary, therefore, to operate under experimental conditions which favor the decomposition expressed by the first equation.

$$C_6H_5N_2SC_6H_5 \longrightarrow N_2 + C_6H_5SC_6H_5 \quad (1)$$

$$C_6H_5N_2SC_6H_5 \longrightarrow N_2 + C_6H_5S_2C_6H_5 \quad (2)$$

Experimental Part

Benzenesulfinic Acid.—This acid was prepared according to a slight modification of the method of Knoevenagel,[15] by passing sulfur dioxide into a mixture of benzene and aluminum chloride. The sodium benzenesulfinate was isolated and recrystallized twice from water. Because of the instability of the free acid it was kept in the form of the sodium salt until shortly before the acid was required, which was then obtained in the usual manner.

_p_-Methoxydiphenylsulfide.—This was prepared after a modification of the Hinsberg method,[8,16] by treating freshly distilled phenol with 2 moles of dry benzenesulfinic acid melting at 83°. Dimethyl sulfate was used as the methylating agent instead of methyl iodide. The crude *p*-methoxydiphenylsulfide was found to contain methylphenylsulfone and an oil which was probably o-methoxydiphenylsulfide. The methylphenylsulfone separated out of the crude distilled oil, from which it was filtered. It was crystallized from a mixture of ethyl alcohol and water and separated in thin plates melting at 88°.

Anal. Calcd. for $C_7H_8O_2S$: S, 20.50. Found: S, 20.48.

This sulfone results from the methylation of benzenesulfinic acid. Its formation was prevented by shaking, before methylation, an ether solution of the crude *p*-hydroxydiphenylsulfide with a solution of sodium carbonate.

The crude p-methoxydiphenylsulfide was purified by repeated fractional distillation

---

[14] Mauthner, *Ber.*, **39**, 1347 (1906).

[15] Knoevenagel, *ibid.*, **41**, 3318 (1908).

[16] See Mauthner, *ibid.*, **39**, 3593 (1906).

and boiled at 194–195° at 13 mm. A 10% yield of a colorless oil having a slight ethereal odor was obtained.

Anal.[17] Calcd. for $C_{13}H_{12}OS$: S, 14.80. Found: S, 14.97.

Attempts to improve the yield by a variation of the proportions of reactants and of the reaction temperature were without success. The use of a catalyst such as calcium chloride increased the amount of resinification.

Demethylation of *p*-Methoxydiphenylsulfide.—Hinsberg[8] used hydrochloric acid at 180° as the demethylating agent. His work was repeated and the method found to be unsatisfactory, because of the poor yield obtained (17.3%). Attempts to improve it by raising the temperature or increasing the amount of hydrochloric acid led to still further decomposition. The use of aluminum chloride to demethylate was investigated and also found to be unsatisfactory.

The use of a solution of hydrobromic acid in glacial acetic acid under pressure proved to be satisfactory, but a simpler and better procedure is to use a mixture of acetic anhydride and 48% aqueous hydrobromic acid in which the use of pressure bottles and the solution of hydrobromic acid in glacial acetic acid is obviated.

Ninety grams of 48% hydrobromic acid was slowly added to 224 g. of acetic anhydride with cooling in an ice–salt bath. Fifty grams of p-methoxydiphenylsulfide was dissolved in this solution, which was contained in a round-bottomed flask provided with a reflux condenser fitted with a calcium chloride tube, and heated at 80–90° for six hours. After completion of the reaction the excess of hydrobromic and acetic acids was removed by distillation under diminished pressure. The remaining oil was treated with a 10% sodium hydroxide solution and heated on a steam-bath for one hour, in order to hydrolyze any acetylated product. After removing the unchanged methoxy compound with ether, the alkaline solution was acidified with hydrochloric acid, when *p*-hydroxydiphenylsulfide separated as an oil. This was extracted with ether and dried over sodium sulfate. After removal of ether, the sulfide was purified by repeated distillation. It boiled at 164–165° at 3 mm. and the yield was 32 g. (68.5%) of a colorless oil, which crystallized in long prisms. They belong to the monoclinic system[18] and have good cleavage into rhomboid fragments. It was recrystallized from petroleum ether, in which it is slightly soluble, and melted at 50–51°. p-Hydroxydiphenylsulfide is exceedingly soluble in alcohol, acetic acid, ether and benzene, and soluble to the extent of 34 parts in 100,000 of water. It gives no color test with ferric chloride and Millon's reagent and yields a yellowish-green color with concentrated sulfuric acid, which turns dark blue on heating. The Folin and Denis phosphotungstic acid reagent[19] gives a positive test.

Anal. Calcd. for $C_{12}H_{10}OS$: S, 15.86. Found: S, 15.64, 15.50.

***p*-Diphenylsulfide-*p*-nitrobenzoate.**—This was prepared by application of the Schotten–Baumann reaction to *p*-hydroxydiphenylsulfide and *p*-nitrobenzoyl chloride. It crystallized from 95% alcohol in large, yellow prisms melting at 74–75°.

Anal. Calcd. for $C_{19}H_{13}O_4NS$: S, 9.19. Found: S, 9.28.

Destruction of the Sulfide Linkage.—Sixteen grams of *p*-methoxydiphenylsulfide was dissolved in 62 g. of a 21% solution of hydrobromic acid in glacial acetic acid and then heated for twenty hours at 60° in a pressure bottle. After removal of excess hydrobromic acid and acetic acid, the remaining oil was shaken with 10% sodium hydroxide solution. A white flocculent precipitate separated which was removed with ether. The ether was distilled off and the solid, after recrystallization from 80%

---

[17] Rogers and Dougherty, THIS JOURNAL, 50, 1231 (1928).

[18] The crystallographic examination was kindly made by Dr. E. J. Roberts.

[19] Folin and Denis, *J. Biol. Chem.*, 12, 240 (1912).

alcohol, was identified as diphenyldisulfide. The above 10% sodium hydroxide solution was acidified with hydrochloric acid, extracted with ether, the ether removed and the remaining oil distilled, which proved to be p-bromophenol.

Refluxing *p*-methoxydiphenyl sulfide with a 48% hydrobromic acid solution also yielded p-bromophenol, diphenyldisulfide and a considerable amount of a resinous product.

Modification of Hinsberg's Reaction to Obtain *p*-Hydrodiphenylsulfide Directly.—By this process the steps of methylation and demethylation and their attendant losses are eliminated. Thirty-two grams (2 moles) of benzenesulfinic acid was mixed with 11.5 g. (1 mole) of phenol and heated on a water-bath for two hours. The dark red reaction mixture was shaken with a sodium carbonate solution and distilled with steam to remove the excess of phenol. The contents of the flask were then acidified with hydrochloric acid, which precipitated a resin and caused an oil to separate. This oil was extracted with ether, the ether extract repeatedly washed with sodium carbonate solution, finally with water and then dried over sodium sulfate. After removal of ether the remaining oil was distilled under diminished pressure; 8 g. of crude *p*-hydroxydiphenylsulfide boiling at 165–167° at 4 mm. was obtained. The yield was 30% of the theoretical. By repeated distillation and crystallization this yield was considerably reduced. Three grams of a pale yellow oil boiling at 160–165° at 4 mm. and which did not crystallize on cooling was also obtained. It is probable that we were dealing here with the ortho isomer of our reaction product, but its structure was not established.

***p*-Methoxydiphenylsulfone.**—A modification of Hinsberg's method[20] for the oxidation of sulfides to sulfones by hydrogen peroxide was used. Ten grams of *p*-methoxydiphenylsulfide dissolved in 100 g. of glacial acetic acid, purified by the method of Orton and Bradfield,[21] was treated with 13 g. of 30% hydrogen peroxide solution. The reaction mixture was allowed to stand at room temperature for one hour and finally heated on a hot-plate for another hour. After the acetic acid had been removed the resulting dark brown oil, which solidified on cooling, was dissolved in hot 60% alcohol, treated with boneblack and the solution cooled, when p-methoxydiphenylsulfoxide and its sulfone crystallized. The sulfone was obtained free from the sulfoxide by recrystallization from alcohol until the product gave no color with concentrated sulfuric acid. *p*-Methoxydiphenylsulfone[22] crystallizes from alcohol in clusters of colorless needles melting at 90–91° and is soluble in ether, benzene, alcohol and insoluble in petroleum ether and water. A yield of 6 g. of the pure sulfone was obtained (52%).

Anal. Calcd. for $C_{13}H_{12}O_3S$: S, 12.92. Found: S, 13.03.

***p*-Hydroxydiphenylsulfone.**—Six grams of p-methoxydiphenylsulfone was dissolved in a mixture of 48% aqueous hydrobromic acid and 20.4 g. of acetic anhydride and heated for six hours at 90°. After removal of the excess of hydrobromic acid and acetic acid, the remaining oil, which solidified on cooling, was treated with a 10% sodium hydroxide solution and extracted with ether. The alkaline solution on acidifying with hydrochloric acid yielded an oil which was dissolved in ether, washed with sodium carbonate solution, water and dried over sodium sulfate. The ether was removed and 3 g, of a brown solid recovered. This was purified by crystallization from alcohol when the sulfone separated in clusters of colorless needles melting at 136–137°. It is difficultly soluble in water and petroleum ether and soluble in hot alcohol and benzene. A water solution gave no color with ferric chloride.

---

[20] Hinsberg, *Ber.*, **41**, 2836, 4294 (1908).

[21] Orton and Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

[22] Böeseken, *Rec. trav. chim.*, **19**, 19 (1900).

Anal. Calcd. for $C_{12}H_{10}O_3S$: S, 13.68. Found: S, 14.08.

p-Hydroxydiphenylsulfide by Application of the Grignard Reaction.—Phenylsulfochloride was prepared from diphenyldisulfide according to the method of Lecher.[9c] This was modified slightly by using carbon bisulfide instead of carbon tetrachloride as the solvent during chlorination. Better results were also obtained by distilling the phenylsulfochloride in an atmosphere of carbon dioxide. It boiled at 60–61° at 3 mm. and the yield was 73.5% of the theoretical.

Twelve and one-half grams (1 mole) of *p*-bromo-anisole was slowly added to 1.75 g. of magnesium turnings in 150 cc. of cold dry ether and the reaction started by means of Gilman's activated magnesium-copper alloy.[23] After refluxing the final reaction mixture for six hours, it was cooled and 9.5 g. of phenylsulfochloride dissolved in 20 cc. of ether slowly added. After the vigorous reaction had subsided, it was digested for an hour on a water-bath and then poured into a mixture of ice and sulfuric acid. The ether layer was separated, washed with 5% sulfuric acid, 5% sodium hydroxide and finally dried over sodium sulfate. After removal of ether the *p*-methoxydiphenylsulfide was distilled and boiled at 161–163° at 6 mm. pressure. The yield was 4.5 g., corresponding to 31.6% of the theoretical.

The p-methoxy phenylsulfide was demethylated according to the directions already given and the resulting *p*-hydroxydiphenylsulfide proved to be identical with that obtained by Hinsberg's method.

Preparation of **p-Methoxydiphenylsulfide by** a Modification of Ziegler's **Method.**[10]—71.5 g. of thiophenol was dissolved in a solution of 50 g. of sodium hydroxide and 300 cc. of water. 100 g. of *p*-anisidine was dissolved in 17 g. of hydrochloric acid and 600 cc. of water and then diazotized in the usual manner with a solution of 56 g. of sodium nitrite in 250 cc. of water. After completion of diazotization a solution of sodium acetate was added to reduce the free hydrochloric acid.

The solution of diazotized anisidine was slowly dropped with constant stirring into the alkaline thiophenate solution which was held at 70°. A yellow precipitate was formed which rapidly decomposed with the evolution of nitrogen and the formation of a brown oil. After the major portion of the diazonium salt solution had been added, the reaction mixture became quite viscous because of the emulsification of the oil. It was finally heated upon a steam-bath for one hour to allow any remaining diazothioether to decompose completely. The final reaction product had a slightly aromatic ethereal odor.

The mixture was then acidified with hydrochloric acid and after adding zinc was refluxed for one hour in order to reduce any diphenyldisulfide to thiophenol, which was removed by distilling with steam. The contents of the flask were cooled and extracted with ether. A brown, solid tar, which was insoluble in acid. alkali or ether remained behind. The brown ether extract was repeatedly washed with 5% sodium hydroxide solution until the alkaline solution no longer turned brown, then with dilute hydrochloric acid, water and finally dried over sodium sulfate. After removal of ether, the remaining oil was distilled when a yield of 67 g. of p-methoxydiphenylsultide was obtained boiling at 150–152° at 3 mm. pressure. This corresponds to 66.0% of the theoretical.

After removal of p-metlioxydiphenylsulfide, the distillation was continued and 11.5 g. of a yellowish-brown oil with a mercaptan odor and boiling over a range of 152–212° at 3 mm. was obtained. Above 212" decomposition set in. From this oil was isolated a solid, which crystallized from 95% alcohol in colorless, matted plates melting at 130–131°. Neither of these substances was further investigated.

An attempt to prepare *p*-hydroxydiphenylsulfide directly by treating sodium thiophenate and diazotized p-aminophenol was unsuccessful.

---

[23] Gilman and Harris, THIS JOURNAL, 49,546 (1927).

o-Methoxydiphenylsulfide.[16]—This was prepared according to a new procedure from sodium thiophenate and diazotized o-anisidine in a manner similar to that described for p-methoxydiphenylsulfide. o-Methoxydiphenylsulfide is a colorless, refractive oil boiling at 150–152° at **3** mm., having a slight aromatic ethereal odor, and was obtained in good yield.

Anal. Calcd. for $C_{13}H_{12}OS$: S, **14.8.** Found: S, **14.52.**

***o*-Hydroxydiphenylsulfide.**[9b]—The o-methoxydiphenylsulfide was demethylated in a manner similar to that described for p-methoxydiphenylsulfide. A yield of 68.5% of o-hydroxydiphenylsulfide boiling at 140° at **3** mm. was obtained. It was a colorless oil with a phenolic odor and resisted all attempts to effect crystallization. Its solubility in various solvents and its color tests were the same as those described for the para-isomer.

Anal. Calcd. for $C_{12}H_{10}OS$: S, **15.85.** Found: S, **15.87, 15.35.**

o-Diphenylsulfide-p-nitrobenzoate was prepared and it crystallized from 95% alcohol in large pale yellowish-green prisms melting at **72–73°.**

Anal. Calcd. for $C_{19}H_{13}O_4NS$: S, **9.19.** Found: S, **9.53.**

***m*-Methoxydiphenylsulfide.**—Diazotized m-anisidine was treated with an alkaline solution of sodium thiophenate in a manner similar to that described for the preparation of p-methoxydiphenylsulfide. In this case the diazothio-ether formed was of a dark red color and the solution rapidly turned dark brown, finally becoming so darkly colored that it was impossible to follow the course of the reaction. As the reaction was taking place there was always a strong odor of aromatic ethers present, evidently due to the formation of m-methoxyphenol. **A** large amount of resin and dyes was also formed. As the diazonium salt of m-anisidine is less stable than those of o- and *p*-anisidine, the yield was correspondingly lower. m-Methoxydiphenylsulfide is a colorless oil boiling at 156° at **4** mm. and the yield was **25.2** g. or 34.7% of the theoretical.

Anal. Calcd. for $C_{13}H_{12}OS$: S, **14.8.** Found: S, **14.72.**

***m*-Hydroxydiphenylsulfide.**—This was prepared by demethylating the above compound with hydrobromic acid. *m*-Hydroxydiphenylsulfide is a colorless oil which has a slight phenolic odor and boils at 159–161° at **3** mm. The solubility and color tests were the same as those for the para-isomer.

Anal. Calcd. for $C_{12}H_{10}OS$: S, **15.85.** Found: S, **15.86.**

m-Diphenylsulfide-p-nitrobenzoate crystallizes from **95%** alcohol in large, yellow plates melting at 103°.

Anal. Calcd. for $C_{19}H_{13}O_4NS$: S, **9.19.** Found: S, **9.28.**

***p*-Methoxy-*p*-methyldiphenylsulfide.**—This was prepared by treating an alkaline solution of sodium thiocresate with diazotized p-anisidine. In this case, however, the oil obtained after removal of the excess of thiocresol solidified on cooling. *p*-Methoxy-*p'*-methyldiphenylsulfide was obtained as an oil boiling at 181–182° at **4** mm. **It** solidified on cooling and was purified by recrystallizing from **95%** alcohol, separating as colorless plates melting at 45–46°. The compound is very soluble in benzene and hot ethyl alcohol.

Anal. Calcd. for $C_{14}H_{14}OS$: S, **13.9.** Found: S, **13.84.**

***p*-Hydroxy-*p*-methyldiphenylsulfide.**—This was prepared from the above methyl ether by demethylation with hydrobromic acid in glacial acetic acid solution. p-Hydroxy-*p'*-methyldiphenylsulfide distilled as a yellow oil boiling at **178–180°** at **3** mm., which quickly solidified on standing. It crystallizes from petroleum ether in colorless, oblong plates melting at 67–68°. **It** is soluble in the common organic solvents and is difficultly soluble in water. **It** gives no color test with ferric chloride.

Anal. Calcd. for $C_{13}H_{12}OS$: S, 14.82. Found: 14.50, 14.52.

General Method for Preparation of Sulfides.—The method as outlined for the preparation of the methoxydiphenylsulfides is not applicable for the preparation of many aromatic sulfides, as many diazonium salts are very unstable at 70° and immediately break down to form the corresponding phenols. A modified method which promises to be applicable for the general preparation of sulfides of the aryl type, was found by using copper as a catalyst for the decomposition of the diazothio-ether.

Fifteen grams of aniline was dissolved in 19.75 g. of concentrated sulfuric acid and 300 cc. of water; 100 g. of ice was added and the mixture diazotized at 0° with a solution of 12 g. of sodium nitrite in 100 cc. of water. The free sulfuric acid was neutralized with sodium acetate.

To a solution of 17.75 g. of thiophenol, 19.3 g. of sodium hydroxide and 100 cc. of water was added 11.5 g. of copper powder. This mixture was constantly stirred during the cooling to 5° and the benzene diazonium salt solution then slowly added through a dropping funnel. The yellow diazothio-ether rapidly broke down with the evolution of nitrogen.

The remainder of this procedure was the same as that for preparing *p*-methoxydiphenylsulfide. After distillation from copper powder, diphenylsulfide was obtained as a colorless oil in a yield of 12.5 g. boiling at 162° at 20 mm.

Preliminary Examination of the Bacteriological Behavior of the Aromatic Sulfide Phenols.—A preliminary investigation of the germicidal activity of the sulfide-phenols described above was made by using B. *typhosum* as the test organism and determining the phenol coefficient according to the method developed by the Hygienic Laboratory.

The same results were also obtained with *p*-hydroxydiphenylsulfide after its aqueous solution had been allowed to stand for one year.

TABLE I

COMPARISON OF ANTISEPTIC STRENGTH OF *p*-HYDROXYDIPHENYLSULFIDE AND PHENOL

Compound	Dilution	Time culture was exposed to action of disinfectant, minutes 2.5	5.0	7.5	10.0	12.5	15.0
Phenol	1:80	−	−	−	−	−	−
Phenol	1:90	+	−	−	−	−	−
Phenol	1:100	+	+	+	−	−	−
Phenol	1:110	+	+	+	+	+	−
Phenol	1:120	+	+	+	+	+	+
p-Hydroxydiphenylsulfide	1:9000	−	−	−	−	−	−
p-Hydroxydiphenylsulfide	1:10000	−	−	−	−	−	−
p-Hydroxydiphenylsulfide	1:11000	+	+	+	−	−	−
p-Hydroxydiphenylsulfide	1:11500	+	+	+	+	−	−
p-Hydroxydiphenylsulfide	1:12000	+	+	+	+	−	−

TABLE II

COMPARATIVE PHENOL COEFFICIENTS

p-Hydroxydiphenylsulfone	Less than	10
o-Hydroxydiphenylsulfide		33
p-Hydroxy-*p*'-methyldiphenylsulfide		50
m-Hydroxydiphenylsulfide		68
p-Hydroxydiphenylsulfide		115

The phenol coefficients of o-hydroxydiphenylsulfide and *p*-hydroxy-*p'*-methyldiphenylsulfide were determined by using them in 20% alcohol solution. Experiments using p-hydroxydiphenylsulfide showed that its phenol coefficient factor was only slightly decreased in 20% alcohol. The phenol coefficient of p-hydroxydiphenylsulfone was shown to be less than 10 and as it consequently could have no use as an antiseptic, work on this was discontinued.

The case of *p*-hydroxy-*p'*-methyldiphenylsulfide represents an anomaly to a quite general rule that an increase in the carbon chain in a phenolic compound increases its bactericidal action. Its phenol coefficient was calculated by the method of Tilley and Schaffer[24] to be about 300.

The antisepticity of the isomeric hydroxydiphenylsulfides increased in the order of ortho, meta and para substitution. This is in agreement with the work of Schaffer and Tilley[25] on the isomeric cresols and cyclohexanols.

A comparison of the results obtained with p-hydroxydiphenylsulfide and p-hydroxydiphenylsulfone indicates that the sulfide linkage is the most favorable construction for stimulating high germicidal activity.[26]

Toxicity of *p*-Hydroxydiphenylsulfide.—The minimum lethal dose on small rabbits was determined by administering with a stomach tube definite weights of p-hydroxydiphenylsulfide until a large enough dose had been given to cause death. These experiments were carried out on young rabbits weighing one pound. Administration of a dose of 1 g. of this sulfur combination produces no apparent effect on the animal. However, when a dosage of 1.4 g. was administered the animal became paralyzed but recovered within twenty-four hours. The test animals died a few hours after the administration of 1.5 g.

The minimum lethal dose for small rabbits, which are no doubt more susceptible than adult rabbits, is 1.5 g. per pound. The phenol is, therefore, comparatively non-toxic. These preliminary toxicity tests were kindly carried out for us by Dr. Paul Pittenger, Pharmacologist, of Baltimore, Maryland.

Summary

1. In this paper are described methods for obtaining in a pure state the three isomeric monophenols of diphenylsulfide.

2. A preliminary bactericidal and toxicity study of the phenols has been made.

3. The p-hydroxydiphenylsulfide shows the highest phenol coefficient of any phenol thus far studied and is a non-toxic substance.

---

[24] Tilley and Schaffer, *J. Bact.*, 12,303 (1926).

[25] Schaffer and Tilley, *ibid.*, 14,259 (1927).

[26] We wish to thank Professor W. L. Kulp and Dr. George Hunt of the Department of Bacteriology for their assistance in the determination of the phenol coefficients.

4. The investigation of the phenol derivatives of aromatic sulfides is being continued in this Laboratory.

New Haven, Connecticut

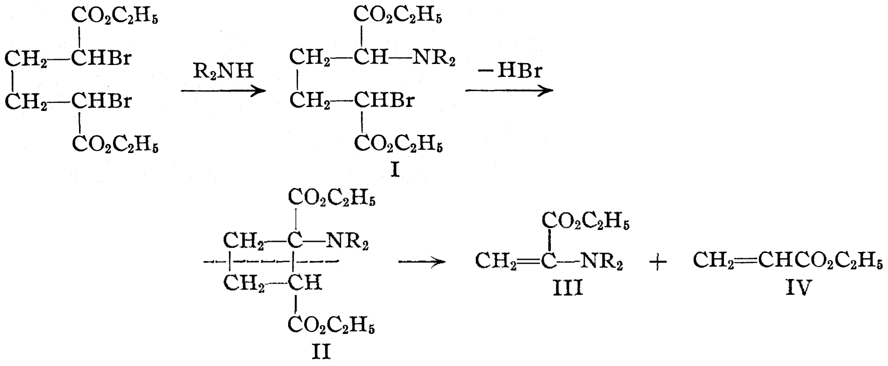
[Contribution from the Chemical Laboratory of the University of Illinois]

THE MECHANISM OF THE CLEAVAGE OF DIETHYL α,α'-DIBROMO-ADIPATE BY SECONDARY AMINES. A NEW SYNTHESIS OF CYCLOBUTANE DERIVATIVES[1]

By Reynold C. Fuson and Tsi Yu Kao

Received December 13, 1928 Published May 6, 1929

According to evidence presented in previous papers by Fuson[2] and Fuson and Bradley,[3] the cleavage of diethyl α,α'-dibromo-adipate by secondary amines discovered by von Braun, Leistner and Münch[4] probably takes place in the following manner



The first step in the reaction is assumed to be the normal replacement of one of the bromine atoms by a dialkylamino group. The cyclobutane intermediate (II) is then produced by the elimination of a molecule of hydrobromic acid. This aminocyclobutane derivative, being unstable under the conditions of the experiment, undergoes dissociation into ethyl acrylate (IV) and ethyl α-dialkylamino-acrylate (III).

The cleavage products actually isolated are ethyl pyruvate and ethyl β-dialkylaminopropionate and are satisfactorily accounted for by the assumption that the α-dialkylamino-acrylic ester is hydrolyzed to the pyruvic ester and that ethyl acrylate unites with the dialkylamine to give the β-dialkylaminopropionic ester.

---

[1] Presented before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 9, 1928

[2] Fuson, This Journal, **50,** 1444 (1928).

[3] Fuson and Bradley, *ibid.*, **51,** 599 (1929).

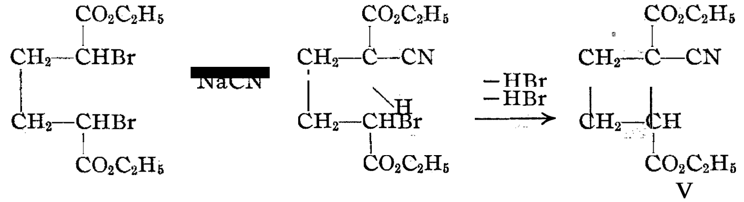
[4] Von Braun, Leistner and Munch, *Ber.*, **59B,** 1950 (1926). See also von Braun, Jostes and Wagner, *ibid.*, **61B,** 1423 (1928).

In an attempt to demonstrate the intermediate existence of II, the authors undertook to prepare it from the corresponding cyclobutanedicarboxylic acid. Although this has as yet not been accomplished, an improved method of synthesis of cyclobutane acids has been worked out which apparently bears out the cleavage mechanism in question. The present article deals with a preparation of the *trans*-1,2-cyclobutanedicarboxylic acid, which not only represents a new type of synthesis but which as intimated above sheds considerable light upon the mechanism of the cleavage of the adipic ester molecule by secondary amines.

It will be noticed that the second step in the mechanism outlined above involves the closure of the cyclobutane ring by the elimination of hydrobromic acid between the two a-carbon atoms. Moreover, since the yield of cleavage products is frequently very high, it is implied by the mechanism in question that the ring closure proceeds smoothly and in good yield. This assumption is at variance with experience inasmuch as closures of the cyclobutane ring by such means have been found to take place with difficulty and generally in small yield.

The authors have made the assumption that the great ease with which the ring closes in this case is due to the presence of the dialkylamino group, which probably activates the hydrogen atom attached to the carbon atom holding the amino group. It is evident that, if the mechanism is the-correct one and if the activation of the hydrogen atom is responsible for the ease of the ring closure, it ought to be possible to carry out the synthesis of cyclobutane derivatives in which the dialkylamino group is replaced by some group known to have an activating effect on the hydrogen atoms on the adjacent carbon atom.

Accordingly, to test these speculations, *meso*-diethyl α,α′-dibromoadipate was treated with sodium cyanide. The expected reactions were as follows



V

The cyclobutane derivative formed in this case (V) should differ from that formed when secondary amines are used (II) only in having a cyano group in place of the dialkylamino group. It was to be expected that V would be more stable than II on this account, and the experiment was undertaken with the hope that V might not undergo the cleavage and so could be isolated and studied.

Experiment has verified these predictions. When refluxed with sodium cyanide, diethyl α,α′-dibromo-adipate gives a 70 to 80% yield of a diethyl 1-cyanocyclobutane-1,2-dicarboxylate which has been shown to have the structure represented by V.

The proof of the structure of V was carried out in the following manner. When this compound was hydrolyzed and the resulting mixture of acids was heated above its melting point, carbon dioxide was eliminated and a mixture of acids was obtained which melted at 98–115°. This mixture, which was assumed to contain the cis- and *trans*-cyclobutane-1,2-dicarboxylic acids, was treated with concentrated hydrochloric acid—a method used by Perkin[5] to transform the cis acid into the tmns isomer. The product after several recrystallizations from concentrated hydrochloric acid melted at 129–130°.[6] By means of a mixed melting-point determination, this acid was shown to be identical with the *trans*-1,2-cyclobutanedicarboxylicacid obtained by Perkin.[5]

The effect of *amino* groups on the stability of cyclobutane derivatives is being investigated.

Experimental Part

Diethyl 1-Cyanocyclobutane-1,2-dicarboxylate.—This ester was obtained when an absolute alcohol solution of *meso*-diethyl-α,α′-dibromo-adipate (m. p. 67°) was refluxed with an excess of sodium or potassium cyanide on the steam-bath. The cyanide used was of commercial grade which had been finely powdered. Preliminary experiments indicated that sodium cyanide gave somewhat better yields than did potassium cyanide and, accordingly, in subsequent work only the sodium cyanide was used. It was found that the progress of the reaction could be followed by testing the solution from time to time for halogen. When the ester no longer showed a positive test for bromine the reaction was complete. A number of runs were made in which the amount of materials used and the time of treatment were varied. The results are shown in the following table.

TABLE I

RESULTS OF RUNS

Run	Refluxing, hours	Abs. ethanol, cc.	NaCN, g.	Bromo-ester, g.	Yield of cyano ester, g.	Yield, %
1	96	15	8	20	8.5	68
2	48	15	8	20	8.6	69
3	48	15	8	20	6.2	50
4	24	25	16	40	19.9	80
5	28	25	16	40	20.0	80
6	30	50	40	100	50.0	80
7	30	25	20	50	22.0	73

There was apparently always a little decomposition, because at the end of the reaction the mixture was dark in color. The dark brown alcohol solution was filtered from the mixture of alkali bromide and unchanged cyanide. The alcohol was removed by distillation at atmospheric pressure and the residual oil was then distilled under

---

[5] Perkin, J. *Chem. Soc.*, 65, 585 (1894).

[6] Perkin gives 131° as the melting point of the *trans* acid.

diminished pressure. It passed over at 160–169° (17 mm.). Redistillation gave a product boiling at 152–154° (9 mm.); d^{20}, 1.1103; n^{20}_{D}, 1.4519.

Anal. Calcd. for $C_{11}H_{15}O_4N$: N, 6.2. Found: N, 6.0%.

Hydrolysis of **Diethyl 1-Cyanocyclobutane-1,2-dicarboxylate.**—The ester was hydrolyzed by hot concentrated barium hydroxide solution (20%) according to Perkin's method.[7] The reaction took place rapidly with the evolution of ammonia. The yield of barium salt is about 85 to 95% of the theoretical.

Preparation of **Trans-cyclobutane-1,2-dicarboxylic Acid.**—The barium salt of the cyclobutane-1,1',2-tricarboxylic acid was treated with slightly less than the theoretical amount of sulfuric acid according to the directions of Perkin. The crude acid, which crystallized from the concentrated water solution after one or two weeks in a vacuum desiccator, was heated above its melting point in an oil-bath whose temperature was maintained at 150° for three to four hours. The brown mass which solidified on cooling was recrystallized from a mixture of benzene and ethyl acetate. The product was nearly colorless.

The crude acid which melts at 98–115° was apparently a mixture of *trans* and *cis* forms. It was treated with concentrated hydrochloric acid at 190° according to Perkin's method in order to convert it into the pure *trans* acid. The acid obtained melted at 129–130° and was shown to be identical with the *trans* acid obtained by the synthesis of Perkin.

Summary

When diethyl-α,α'-dibromo-adipate is treated with sodium cyanide, it is converted into diethyl 1-cyanocyclobutane-1,2-dicarboxylate, which on being hydrolyzed loses carbon dioxide to yield a mixture of acids. On treatment with concentrated hydrochloric acid, this mixture is converted into *trans*-cyclobutane-1,2-dicarboxylic acid. The identity of the latter has been established by comparison with a specimen of this acid prepared by the method of Perkin.

This synthesis is interpreted as evidence in favor of the cyclobutane mechanism proposed for the cleavage of diethyl α,α'-dibromo-adipate by secondary amines.

URBANA, ILLINOIS

---

[7] Perkin, *J. Chem. Soc.*, 65, 580 (1894).

[CONTRIBUTION PROM THE LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE PREPARATION AND PROPERTIES OF THE ISOMERIC HEPTANES. PART II. PHYSICAL PROPERTIES

BY GRAHAM EDGAR AND GEORGE CALINGAERT

RECEIVED DECEMBER 20, 1928 PUBLISHED MAY 6, 1929

I. Introduction

In Part I of this paper[1] the preparation and purification of the nine isomeric heptanes were reported, together with certain data on the physical properties commonly employed for purposes of identification. In Part II there are presented measurements obtained in this Laboratory on other properties, together with a summary of the data of other investigators to whom samples of these hydrocarbons were loaned. Some of these data have been published and others are presented prior to publication elsewhere by the courtesy of the investigators in question, to whom acknowledgment is made below. The entire available data are summarized for the purpose of discussing the effect of structure upon the physical properties, since few trustworthy data are available on this point for the paraffin hydrocarbons and since the group in question is large enough to cover a wide variety of structural types. Further data are being accumulated on other properties of these hydrocarbons, but as the results of these investigations seem likely to be unavailable for some time to come, it has not been thought advisable to delay further the present publication.

II. Experimental Methods

(a) Densities, boiling and melting points are discussed in Part I of this paper.

The data on refractive indices, dispersions, dielectric constants and viscosities are taken from Smyth and Stoops,[2] where data additional to those quoted herein may be found.

(b) Surface tensions were measured in this Laboratory, employing essentially the technique of Richards, Speyers and Carver.[3]

In order to check the accuracy of the data, measurements were made of the surface tension of normal octane, which agreed well with those of Richards, Speyers and Carver, and of pure benzene, which agreed well with the data in "International Critical Tables." The measurements were made at one or more temperatures within a degree or two of 20°, and were extrapolated to this temperature.[4]

---

[1] Edgar, Calingaert and Marker, THIS JOURNAL, 51, 1483 (1929).

[2] Smyth and Stoops, *ibid.*, 50, 1883 (1928).

[3] Richards, Speyers and Carver, *ibid.*, 46, 1196 (1924).

[4] These measurements were made by Mr. F. J. Dykstra, to whom the authors are indebted. The authors also desire to acknowledge the loan of a cathetometer for this work by the Department of Physics of New York University.

(c) Critical temperatures and pressures were measured by Professor F. G. Keyes and Dr. R. V. Kleinschmidt, to whom the authors are much indebted both for the measurements and for permission to include the data in this paper, prior to publication elsewhere. The apparatus and technique were essentially those described by Keyes, Taylor and Smith.[5] At the time these measurements were made, 3,3-dimethylpentane had not been prepared and no critical data concerning it are available. The coefficient *a* and b of van der Waals' equation (Cols. 12 and 13) were calculated from these data, as were the values of the Guldberg function T_c/T_B (Col. 11).

(d) The coefficients of thermal expansion were measured in this Laboratory by Mr. O. R. Dorion, to whom the authors are indebted. The apparatus consisted of a dilatometer of Pyrex glass, with a bulb of about 6 cc. capacity and a capillary of such dimensions as to give about 30 cm. rise in the liquid level of the hydrocarbons for 20" temperature rise. The dilatometer was calibrated by filling it with a known weight of distilled water and reading the liquid level in the capillary at different temperatures, readings being made with a cathetometer. Density data for water were taken from "International Critical Tables," and appropriate corrections were made for the thermometer employed and for the expansion of the glass. The dilatometer was then filled with weighed amounts of the hydrocarbons and the liquid level in the capillary was measured at various temperatures from 10 to 30°. Since for the purpose of this paper the relative coefficients of expansion of the hydrocarbons were more important than their absolute values, the following method was employed in treating the data. The liquid level readings in the capillary were plotted on large scale coordinate paper against the temperature and from the curves thus obtained temperature differences were read corresponding to the same definite segment of the capillary between two fixed marks. The bulb was in all cases filled to such an extent that the segment corresponded approximately to the temperature range of 15 to 20°. The hydrocarbons are so nearly alike in their expansion coefficients that the actual temperatures involved were seldom as much as a degree different for the different hydrocarbons. A value for the coefficient of expansion of normal heptane was then selected as a mean from density determinations at temperatures above and below 20° by the authors (Part I), from the data of Smyth and Stoops[2] and from the dilatometer dimensions. The values for the isomers were then computed by comparing the temperature differences above mentioned with that for normal heptane. The data are given to four significant figures and are almost certainly correct to three. The supply of 3,3-dimethylpentane was exhausted when these measurements were made, and its density–temperature coefficient was taken as the average for the other eight isomers, that is, 0.000848. This value is probably very nearly correct,

---

[5] **Keyes, Taylor and Smith, J.** *Math. Phys., Mass. Inst. Tech., 1, 311* **(1921).**

since it is equal to that of the 2,3-isomer, which, as will be shown in the discussion below, shows properties very similar to those of the 3,3-isomer.

The temperature coefficients of density in the neighborhood of 20" had already been determined for most of the hydrocarbons, but it was felt that values calculated from the coefficients of thermal expansion were more nearly accurate than the direct measurements, and the figures in Col. 4 are calculated in this way.

(e) The velocity of sound through the hydrocarbons and the coefficient, β_φ, of adiabatic compressibility, were measured by E. B. Freyer, J. C. Hubbard and D. H. Andrews.[6]

The coefficients of isothermal compressibility, β_T, were calculated by the equation $\beta_T = \beta_\varphi + \dfrac{(\mathrm{d}v/\mathrm{d}t)^2\,\mathrm{d}T}{J\,C_p}$, where J is the mechanical equivalent of heat, C_p the specific heat, v the specific volume and d the density. In the absence of specific heat data for most of the isomers the value of 0.50 cal. per g. for normal heptane was employed in all calculations. Later data on actual specific heats may alter the computed values slightly.

(f) Heats of combustion were determined by the U. S. Bureau of Standards.[7] They were made in a bomb calorimeter and are defined as the heat liberated in 20° calories per gram of liquid hydrocarbon weighed in air, the products of combustion being cooled to the initial temperature and the water condensed to the liquid state. The data are believed to be accurate to 0.2% or better.

(g) Molecular diameters and lengths were calculated by Stewart from X-ray diffraction data.[8]

(h) Critical solution temperatures in aniline were determined in this Laboratory. Aniline was dried over solid potassium hydroxide and was freshly distilled before each determination. The hydrocarbons were also dried over solid potassium hydroxide.

The mixtures of aniline and hydrocarbon were heated in a small test-tube fitted with an Anschütz thermometer, the whole being jacketed by another test-tube, which in turn was immersed in a water-bath. The aniline and hydrocarbon were weighed into the test-tube and the weight was checked after the determination in order to ascertain whether appreciable loss due to volatilization of hydrocarbon had occurred. The proportions of aniline and hydrocarbon were altered through a range sufficient to pass through the maximum point on the solubility–temperature curve.[9] The data are expressed graphically in Fig. 1.

---

[6] **Freyer, Hubbard and Andrews, THIS JOURNAL, 51, 759 (1929).**

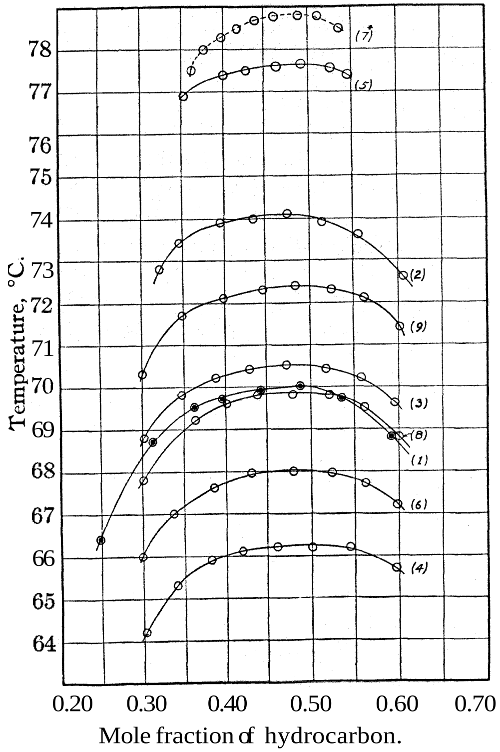
[7] **Bureau of Standards Journal of Research, 2, 373 (1929).**

[8] **S. W. Stewart, Phys. *Rev.*, 32, 153 (1928).**

[9] **These determinations were made by Mr. D. T. Mood, to whom the authors are indebted.**

III. Experimental Data

Table I contains the experimental data referred to above, together with certain functions derived from the data. Table II summarizes the order in which these properties and functions vary with the structure of the hydrocarbons. Table III contains such data as are available from the literature on the properties of the hexanes, octanes, nonanes and decanes. Only such data are given as are available for a number of the isomers, since the data are used for comparison of the effect of structure on the properties of the hydrocarbons as compared with the heptanes. The data have been taken from what seemed to be the most reliable sources, some from "International Critical Tables," some from Beilstein and some from the original literature. The data have been extrapolated when necessary.



(1), *n*-**Heptane**; (2), 2-methylhexane; (3), 3-**methylhexane**; (4), 3-ethylpentane; (5), 2,2-dimethylpentane; (6), **2,3-dimethylpentane**; (7), **2,4-dimethylpentane**; (8), **3,3-dimethylpentane**; (9), **2,2,3-trimethylbutane.**

Fig. 1.—Critical solution temperatures of the heptanes in aniline.

* Because of the extremely small amount of **2,4-dimethylpentane** which was available when these measurements were made it was not possible to determine accurately the values of the mole-fractions corresponding to the temperatures given. The curve must therefore be regarded as approximate as far as the mole-fraction data are concerned.

IV. Discussion

(a) **General.**—Very few of the data given in Table I are available in the literature. With the exceptions noted in Part I of this paper, the data in general agree very well with the most reliable data which are available. Since the chief purpose of this paper is to discuss the effect of structure upon physical properties, further comparison of the individual data with those in the literature has been omitted.

Very few generalizations have been possible heretofore concerning any relations which may exist between the structure of paraffin hydrocarbons

TABLE IA

PHYSICAL PROPERTIES OF THE HEPTANES

No.	Name	(1) B. p., °C. (760 mm.)	(2) M. p., °C.	(3) d_4^{20}	(4) $\Delta d/\Delta t$ (20°C.)
1	*n*-Heptane	98.4	− 90.5	0.6836	0.000835
2	2-Methylhexane	90.0	−119.1	.6789	.000855
3	3-Methylhexane	91.8	.....	.6870	.000844
4	3-Ethylpentane	93.3	.....	.6984	.000853
5	2,2-Dimethylpentane	78.9	−125.6	.6737	.000855
6	2,3-Dimethylpentane	89.7	.....	.6952	.000848
7	2,4-Dimethylpentane	80.8	−123.4	.6745	.000856
8	3,3-Dimethylpentane	86.0	−135.0	.6934	.000848[a]
9	2,2,3-Trimethylbutane	80.9	− 25.0	.6900	.000838

[a] Assumed value, see paragraph d, section II.

TABLE IB

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(5) $n_D^{20°}$	(6) MR_D	(7) $MR_\gamma - MR_\alpha$	(8) Dielec. const. ϵ, at 20°	(9) t_c, °C.	(10) P_c, atm.	(11) T_c/T_B	(12) $a \times 10^{-7}$ (van d. Waals)
1	1.38777	34.54	0.84	1.930	269.5	27.65	1.460	3.025
2	1.38509	34.57	.85	1.922	257.9	27.2	1.462	2.945
3	1.38873	34.45	.83	1.930	262.4	28.1	1.467	2.900
4	1.39366	34.27	.82	1.942	267.6	28.6	1.479	2.905
5	1.38233	34.61	.86	1.915	247.7	28.4	1.480	2.727
6	1.39201	34.31	.83	1.942	264.6	29.2	1.493	2.814
7	1.38233	34.57	.85	1.917	247.1	27.4	1.470	2.813
8	1.39114	34.32	.83	1.940	...	...	...	...
9	1.38940	34.35	.84	1.930	258.3	29.75	1.497	2.697

n = index of refraction. MR = $(n^2-1)/(n^2+2) \times 1/d$. $MR_\gamma - MR_\alpha$ = molecular dispersion for the hydrogen α and γ lines.

TABLE IC

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(13) b (cc) van d Waals	(14) a/V^2	(15) Vel. of sound at 20° m/sec.	(16) β_φ (20°) atm. × 10^6	(17) β_T (20°) × 10^6	(18) $\alpha \times 10^5$	(19) $\alpha/\beta_T \times 293$	(20) $(5200+30t_B)/V$
1	201.4	1415	1154.0	111.4	142.37	122.2	2513	55.73
2	200.3	1358	1120.0	119.05	152.20	125.9	2424	53.62
3	195.5	1368	1135.5	114.45	145.62	122.8	2471	54.64
4	193.9	1417	1169.5	106.15	136.46	122.2	2621	55.87
5	188.1	1232	1080.0	128.90	162.79	126.8	2282	50.98
6	188.9	1360	1148.5	110.70	140.68	122.0	2541	54.86
7	194.8	1280	1083.5	128.00	161.85	126.8	2296	51.42
8	...	...	1129.5	114.55	145.13	122.3[a]	2467	53.95
9	183.2	1284	1101.5	121.05	151.44	121.5	2351	52.63

[a] Assumed value.

V = the molecular volume. β_φ = the adiabatic compressibility in cc./cc./atm. β_T = the isothermal compressibility in cc./cc./atm. α = the coefficient of thermal expansion in cc./cc./°C.

TABLE ID

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(21) Surf. tens., 20°, γ,dynes/cm.	(22) $\gamma/V^{1/3}$	(23) C T S, aniline, °C.	(24) η 20°	(25) Mol. diam., cm. × 10^8	(26) Mol. length, cm. × 10^8	(27) Ht. of comb., cal./g.
1	20.28	3.848	70.0	0.00409	4.64	11.38	11490
2	19.37	3.668	74.1	.00378	4.84, 5.25	10.47, 8.87	11480
3	19.56	3.718	70.5	.00372	5.68	7.46	11480
4	20.16	3.854	66.3	.00377	5.51	7.84	11490
5	17.80	3.362	77.7	.00385	5.68	7.61	11470
6	19.65	3.750	68.1	.00406	5.68	7.38	11480
7	17.93[a]	3.388[a]	78.8	.00361	5.68	7.61	11480
8	19.63	3.743	71.0	.00454	5.68	7.38	11470
9	18.60	3.541	72.4	.00585	5.69	7.45	11470

γ = the surface tension in dynes per cm. η = the absolute viscosity. C.T.S. aniline = the critical solution temperature in aniline at the concentration giving the maximum temperature.

[a] There is some uncertainty as to the state of purity of the sample used for this particular measurement. The data, however, fall in an order which agrees with the other properties.

TABLE II

ORDER IN WHICH THE PHYSICAL PROPERTIES OF THE HEPTANES VARY

1 = lowest value; h = highest value

(a)	d	5	7	2	1	3	9	8	6	4	1 — h
	n_D	(5	7)	2	1	3	9	8	6	4	1—h
	MR	5	7	2	1	3	9	8	6	4	1 — h
	$Mr_\gamma - MR_\alpha$	5	(7	2)	(1	9)	(3	8	6)	4	I—h
	ϵ	5	7	2	(1	3	9)	8	(6	4)	1—h
(b)	$\gamma/V^{1/3}$	5	7	9	2	3	8	6	1	4	1—h
	$(5200-30t_B/V)$	5	7	9	2	8	3	6	1	4	1—h
	a/V^2	5	7	9	2		6	3	1	4	1—h
	α/β_T	5	7	9	2	8	3	1	6	4	1—h
	C.T.S.	7	5	2	9	8	3	1	6	4	h—1
(c)	γ	5	7	9	2	3	8	6	4	1	1 — h
	β_φ	5	7	9	2	3	8	1	6	4	h—1
	β_T	5	7	2	9	3	8	1	6	4	h—1
	Vel. sound	5	7	9	2	3	8	6	1	4	1 — h
	T_c	5	7	2	9	3		6	4	1	1—h
	B. p.	5	7	9	8	6	2	3	4	1	1 — h
(d)	P_c	2	7	1	3	5	4	6	9		1—h
	a	9	5	7	6	3	4	2	1		1—h
	b	9	5	6	4	7	3	2	1		I—h
	T_c/T_B	9	6	5	4	7	3	2	1		h—1
	η	7	3	4	2	5	6	1	8	9	1 — h

(a), Density, refraction, dielectric properties and functions; (b), functions and properties directly measuring internal pressure; (c), properties and functions relating to internal pressure and following essentially the same order; (d), miscellaneous properties and functions.

TABLE III

PHYSICAL PROPERTIES OF HEXANES

* = Extrapolated

No.	Name	B. p., °C.	d_4^{20}	n_D^{15}	η_{20}	C T S. Aniline	Compr. (20°) 100–300 atm.
1	n-Hexane	68.95"	0.6595^{*b}	1.3760^{*c}	0.00320^{d}	68.9"	117.5'
2	2-Methylpentane	60.2"	$.6542^{*a}$	1.37445^{b}	$.00310^{d}$	74.7"	119.0"
3	3-Methylpentane	63.2^{a}	$.6647^{*a}$	1.37929^{b}	$.00322^{d}$	69.4"	...
4	2,2-Dimethylbutane	49.7"	$.6498^{*a}$	1.37158^{b}	$.00375^{d}$	80.75"	...
5	2,3-Dimethylbutane	58.1^{a}	$.6618^{*a}$	1.38092^{b}	$.00385^{d}$	72.3"	..

PHYSICAL PROPERTIES OF OCTANES

No.	Name	B. p., °C.	d_4^{20}	n_D^{20}	C.T.S. aniline	Compr. (20°) 100–300 atm.	η_{20}
1	n-Octane	124.6"	0.702^{*c}	1.3980"	72.0^{h}	95.7"	21.88^{g}
2	2-Methylheptane	116.0^{c}	$.6985^{i}$	1.3935^{i}	74.0^{h}	101.0"	20.98^{g}
3	3-Methylheptane	122.2"	$.707^{c}$	.....	...	....	...
4	4-Methylheptane	118.0^{c}	$.722^{c}$	1.398^{c}	...	....	...
5	3-Ethylhexane	118.8"	$.713^{*i}$	1.4016^{c}	...	96.0	
6	2,3-Dimethylhexane	114.0^{c}	$.720^{*c}$	1.4093"	...	....	...
7	2,4-Dimethylhexane	109.9'	$.703^{*c}$	1.4026'	. .	....	
8	2,5-Dimethylhexane	109.2'	$.696^{*i}$	1.3929^{c}	...	105.0^{e}	20.02^{g}
9	3,4-Dimethylhexane	116.5'	$.721^{c}$	1.4058^{c}	...	94.5^{e}	. .
10	2-Methyl-3-ethylpeatane	114.0'	$.704^{*c}$	1.4016^{c}	...	....	...
11	2,2,3-Trimethylpentane	110.8'	$.717^{*c}$	1.4184'	...	....	...
12	2,2,4-Trimethylpentane	99.3^{j}	$.6918^{k}$	1.3916^{k}	...	....	...

PHYSICAL PROPERTIES OF THE NONANES

No.	Name	B. p., °C.	d_4^{20}
1	n-Nonane	150.6^{c}	0.718^{c}
2	3-Methyloctane	143.4"	$.719^{*c}$
3	4-Methyloctane	141.6"	$.727^{*c}$
4	4-Ethylheptane	139.0^{c}	$.737^{*c}$
5	3,3-Diethylpentane	139.2^{l}	$.7522^{l}$
6	2,4-Dimethylheptane	133.3'	$.716^{*c}$
7	2,5-Dimethylheptane	135.9"	$.714^{*c}$
8	2,6-Dimethylheptane	132.0^{c}	$.707^{*c}$
9	2,2,5-Trimethylhexane	126.0^{i}	$.707^{*i}$

PHYSICAL PROPERTIES OF THE DECANES

No.	Name	B. p., °C.	d_4^{20}
1	n-Decane	174.0^{c}	0.730^{*i}
2	2-Methylnonane	160.0^{c}	$.724^{*c}$
3	3-Methylnonane	166.9"	$.735^{c}$
4	5-Methylnonane	166.2"	$.732^{c}$
5	4-Propylheptane	161.7'	$.736^{*c}$
6	2,6-Dimethyloctane	160.5'	$.729^{i}$
7	2,7-Dimethyloctane	160.0^{c}	$.722^{c}$
8	3,6-Dimethyloctane	160.8"	$.730^{*c}$
9	2,2,6-Trimethylheptane	152.0'	$.721^{i}$

[a] Chavanne, *Bull. soc. chim. Belg.*, 31, 331 (1922); [b] Lowry, *J. Chem. Soc.*, **105**, 91 (1914); [c] "International Critical Tables;" [d] Chavanne and van Risseghem, *Bull.*

and their physical properties, since the experimental data have been very fragmentary and none too reliable. Most generalizations previously reported have referred to the effect of increasing molecular weight in the normal hydrocarbons, to such facts as that the boiling point of the normal hydrocarbon is higher than those of the known isomers and to a few scattered facts concerning the relations between the normal hydrocarbon and the simple "iso"-hydrocarbons. The data herein presented give an opportunity for a much more complete analysis of such relationships.

Thus inspection of Tables I and II shows certain striking regularities in the order in which the physical properties vary with the structure. For the purpose of simplifying the discussion each hydrocarbon has been given a number, and the structures corresponding to these numbers are contained in Table I.

(b) Density, Refraction and Dielectric Constant.—If we consider first density, index of refraction and dielectric constant, the isomers fall in an order which is essentially identical for all the properties. The order is still noticeable in properties which are known with less accuracy, coefficient of expansion and dispersion, and even in functions calculated from these constants and which are considered in general to be independent of structure, molecular refraction, molecular dispersion and polarization.

It would seem, therefore, that they must correspond to a definite influence of the structural arrangement of the atoms in the molecule. Thus the values of each function of this group for the normal hydrocarbon occupy an intermediate position. A methyl group located in the 2-position decreases the value of each function below that of the normal hydrocarbon, while a methyl group located in the 3-position increases the value of each function. Similarly, two methyl groups in the 2-position (either on the same carbon atom, or at corresponding positions at each end of the pentane chain) decrease still further the values of the function, while two methyl groups in the 3-position, or an ethyl group in the 3-position, increase still further the values of the functions above those of the normal hydrocarbon. When two groups are adjacent, however, the values of the various functions are always quite high relative to the normal. This effect appears in 2,3-dimethylpentane and in 2,2,3-trimethylbutane, and will be discussed further below.

The order in which the hydrocarbons fall when arranged in accordance with the variation of their properties of this group is essentially 5 7 2 1 3 9 8 6 4, which will be referred to as Order 1.

---

soc. chim. Belg., 31, 87 (1922); [e] Richards, Steel, Mathews and Speyers, THIS JOURNAL, 34, 971, 988 (1912); [f] van Risseghem, Bull. *soc. chim. Belg.*, 31, 62 (1922); [g] Hildebrand, "Solubility," The Chemical Catalog Company, Inc., New York, 1924; Stewart, *Phys. Rev.*, 32, 153 (1928); [h] Chavanne and Simon, *Compt. rend.*, 168, 1112, 1324 (1919); [i] Beilstein, 4th ed., Suppl., Vol. I; [j] Graham Edgar, *Ind. Eng. Chem.*, 19, 145 (1927); [k] Smyth and Stoops, THIS JOURNAL, 50, 1883 (1928); [l] Morgan, Carter and Duck, J. *Chem. Soc.*, 127, 1252 (1925); Lowry, *ibid.*, 127, 1215 (1925).

(c) Internal Pressure.—It has been shown by Hildebrand[10] that relative internal pressures may be calculated approximately from surface tension, from the boiling point, from van der Waals' constant, a, from the ratio of the coefficients of thermal expansion to isothermal compressibility and from the critical solution temperatures in a non-polar solvent. If we consider these various functions (Cols. 19, 20, 22 and 23), we find the isomers falling in a nearly identical order 5 7 9 2 8 **3** 6 1 4, which will be referred to as Order 2.

Considering the uncertainty underlying the assumptions involved in the calculation of these functions, the agreement in Order 2 is striking.

As would be expected, the fundamental properties employed in the calculation of the internal pressures (Cols. 1, 9, 15, 16, 17 and 21) follow in general the same order, with somewhat greater variation, particularly with reference to the normal hydrocarbon, which varies between the extreme end position and the third position from the end.

(d) Van der Waals' constants a and b follow an order very close to that of the ratio of the critical temperature to the boiling point, which may indicate that their values vary with the temperature, and at corresponding temperatures might fall in line with the other properties.

(e) The critical pressures and the viscosities show no evidence of relation to any other property.

(f) The heats of combustion are clearly identical within the limit of error, 0.2% or 2000 cal. per mole. The heats of formation calculated therefrom are thus also identical, their value being 57,000 ± 2000 cal. Obviously the experimental accuracy is not sufficient to determine whether or not small differences exist among the heats of formation of the isomers. It has been shown by Parks[11] that in the case of three isomeric octanes very substantial differences exist in the entropies, but the differences in the heats of formation must be small, if they exist at all.

(g) Regarding the arrangement of the atoms in space, some conclusions may be drawn from the X-ray diffraction data of Stewart. The addition of methyl or ethyl groups as side chains decreases the apparent length of the main chain and increases the apparent diameter by more than would be expected. It seems probable, therefore, that the substitution causes a twisting or bending back of the otherwise straight chain. The only exception to this rule is 9, in which the butane chain keeps its normal length. This is also the only case which has been investigated in which every carbon between the ends of the chain is substituted, which suggests that in that case the bending of the chain may be hindered by the closely packed side chains.

---

[10] Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, 1924.

[11] G. S. Parks, paper delivered at American Chemical Society meeting at Swampscott, Massachusetts, September, 1928.

(h) It will be noted that the difference between Order 1 and Order 2 is entirely due to the change of position of the normal hydrocarbon (1) and the 2,2,3-trimethylbutane (9). If these two be omitted, the order of variation of the properties of both classes becomes surprisingly constant. These two compounds represent, of course, the two extremes of structural arrangement; nevertheless, the cause of their variation from the general arrangement is not clear.

It is interesting to speculate on the reasons for this orderly variation of physical properties with structure. From the thermodynamic standpoint no data are at present available, although it is hoped that the entropies of these compounds will be determined later. Judging from the data of Parks on three octanes,[11] the entropies of the branched-chain isomers should be lower than those of the normal hydrocarbons, but the relation to structure cannot be more than guessed at.

(i) Hydrocarbons other than the **Heptanes.**—The data discussed above for the heptanes is particularly useful for determining the effect of structure, because of the fact that each individual property was measured for all of the isomers by one experimenter, and hence the data are much more comparable than most of those given in the literature and taken from scattered sources. Nevertheless, consideration of the data in Table III on the properties of the hexanes, octanes, nonanes and decanes shows that the considerations indicated above for the heptanes hold very well for the other hydrocarbons.

Thus a methyl group in the 2-position decreases the specific gravity and refractive index below the normal hydrocarbon (with the exception of the hexanes, the data on refractive index are somewhat uncertain, and have been omitted entirely for the nonanes and decanes), while a methyl group in the 3-position increases these functions above that of the normal hydrocarbon. Two methyl groups in the 2-position (2,2-dimethylbutane, 2,5-dimethylhexane, 2,6-dimethylheptane and 2,7-dimethyloctane) decrease still further the specific gravity, while 2,3-dimethylbutane shows the effect of adjacent carbon atoms, as do 2,3- and 3,4-dimethylhexane.

Three methyl groups in the 2-position (2,2,4-trimethylpentane, 2,2,5-trimethylhexane and 2,2,6-trimethylheptane) have the lowest specific gravities reported, but when the groups are adjacent, as in the corresponding 2,2,3-trimethylbutane, the latter effect predominates.

In the octanes, nonanes and decanes a methyl group in the 4- or 5-position has an effect similar to one in the 3-position. An extreme case of the effect of substitution in the 3-position is shown by 3,3-diethylpentane.

Such other properties as are available agree well with the order of variation shown by the heptanes. Thus for the hexanes the critical solution temperatures in aniline follow the order shown for corresponding heptanes, as do the two which are available for the octanes. The available compressibilities and surface tensions follow the usual order, while the viscosities (available only for the hexanes) show the irregular variation exhibited by the heptanes.

The boiling points of the normal hydrocarbons are invariably the highest for the isomers, but the 2-substituted isomers always boil lower than the 3-substituted isomers, and those containing two or three methyl groups in the 2-position (at the same or opposite ends of the chain) boil lowest of all.

Altogether, although the data on the other paraffin hydrocarbons are not sufficiently complete to lay down any definite laws relating their structure to their properties, it is clear that so far as the data are available the regularities found in the heptanes are also found in the other hydrocarbons. It would appear probable, therefore, that approximate values of most of the physical properties of the paraffin hydrocarbons can be predicted with reasonable assurance when their structure is known.[12]

It is hoped that this investigation may be helpful in interpreting the characteristics of the paraffin hydrocarbons, and may eventually lead to clarifying these characteristics in terms of the energy relations and molecular dimensions involved.

Summary

1. Data on a number of the physical properties of the nine isomeric heptanes are presented, together with functions derived from the data.

2. Certain definite regularities are found relating the physical properties of the isomers to their structure.

3. The relationships between the structure of the heptanes and their physical properties exist also for the hexanes, octanes, nonanes and decanes, as far as the data are available.

4. These relationships enable the physical properties of paraffin hydrocarbons to be predicted with reasonable assurance from their structures.

YONKERS, NEW YORK

---

[12] An interesting example of such prediction is found in the case of normal decane. The specific gravity given in "International Critical Tables," Vol. I, seemed to the authors to be probably too high, as it is greater than that of any of the isomers. Examination of the literature confirmed this suspicion, and judging from the data on normal decane in Vol. III of "International Critical Tables," the value of the density in Vol. I is really for 0° instead of 20° as stated.

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, PULP AND PAPER RESEARCH INSTITUTE, MCGILL UNIVERSITY]

SYMMETRICAL TETRABROMO-ETHYL ETHER AND "SO-CALLED" TETRABROMOBUTYRALDEHYDE

BY HAROLD HIBBERT, STANLEY Z. PERRY* AND K. AUSTIN TAYLOR[2]

RECEIVED DECEMBER 28, 1928 PUBLISHED MAY 6, 1929

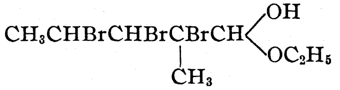
Freundler,[3] in the preparation of bromo-acetaldehyde by the bromination of paracetaldehyde isolated a crystalline product which from the analysis he was led to believe was tetrabromobutyraldehyde ($CH_2BrCHBrCBr_2CHO$), although as specifically pointed out by him, the compound possessed none of the usual aldehydic properties. He assumed that it was formed by the crotonization of the bromo-acetaldehyde, followed by addition of a second mole of bromine

$$2CH_2BrCHO \longrightarrow CH_2BrCH{=}CBrCHO + H_2O$$
$$CH_2BrCH{=}CBrCHO + Br_2 = CH_2BrCHBrCBr_2CHO$$

The same type of reaction is indicated in the work of Kramer and Pinner[4] and of Freundler[5] on the chlorination of acetaldehyde. The trichlorobutyraldehyde isolated by these workers is presumably formed from the primary monochloro-acetaldehyde by condensation of this with acetaldehyde, followed by crotonization and subsequent addition of chlorine:

$$CH_3CHO + Cl_2 = CH_2ClCHO + HCl$$
$$CH_3CHO + CH_2ClCHO = CH_3CH{=}CClCHO + H_2O$$
$$CH_3CH{=}CClCHO + Cl_2 = CH_3CHClCCl_2CHO$$

More recently, Dworzak and Pfifferling,[6] by brominating parapropionaldehyde and treating the reaction mixture with alcohol, obtained a compound, the analysis and molecular weight of which corresponded to the half acetal



$$CH_3CHBrCHBr\underset{\displaystyle CH_3}{\underset{|}{C}}BrCH\left\langle\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$$

apparently formed by a series of reactions similar to those above. This type of reaction, therefore, appears to be a general one.

However, while the other halogenated aldehydes referred to above possess characteristic aldehydic properties, and there would seem to be no

---

[1] Candidate for the Master of Science degree, McGill University.

[2] Holder of Abitibi Power and Paper Co., Ltd., Fellowship, McGill University, Montreal. The authors' best thanks are due to the Abitibi Power and Paper Co., Ltd., for the donation of a Fellowship to one of the authors (K. A. T.) and to the Canadian Pulp and Paper Association for valuable financial assistance.

[3] Freundler, *Compt. rend*, 140, 794, 1693 (1905); Bull. *soc. chim.*, [4] 1, 71 (1907).

[4] Kramer and Pinner, Ber., 3, 383 (1870); *ibid.*, 8, 1561 (1875).

[5] Freundler, Bull. *soc. chim.*, [4] 1, 68, 201, 203 (1907).

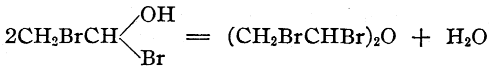
[6] Dworzak and Pfifferling, *Monatsh.*, 48, 255 (1927).

reason to doubt the structures assigned to them, these same properties are entirely absent in the case of the tetrabromobutyraldehyde isolated by Freundler.

From a consideration of the polarities of the groups present, and of the effect of strongly negative groups, such as Br, on the reactivity of the carbonyl group,[7] it is to be expected that a compound such as Freundler's tetrabromobutyraldehyde would show a remarkable degree of reactivity, especially with regard to properties associated with the aldehyde group.

Further evidence against the aldehydic formula is available from Freundler's data. Heating with alcohol gave ethyl bromide, bromo-acetaldehyde and bromo-acetal. Cold fuming nitric acid oxidized it, giving bromo-acetic acid and hydrobromic acid but no tetrabromobutyric acid. These are not the reaction products one would expect from tetrabromobutyric aldehyde.

Stepanov, Preobrashenski and Shchukina,[8] in continuing the work of Hibbert and Hill[9] on the bromination of paracetaldehyde, pointed out that the tetrabromo compound of Freundler might possibly be tetrabromoethyl ether, formed by the loss of water from two moles of bromo-acetaldehyde bromohydrin

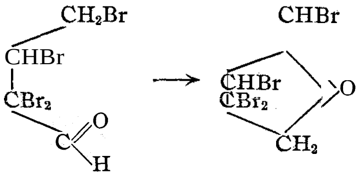


$$2CH_2BrCH\begin{matrix}OH\\Br\end{matrix} = (CH_2BrCHBr)_2O + H_2O$$

A B

the intermediate addition compound (A) actually being isolated by them. This reaction is thus similar to the formation of dichloro-ethyl ether by the action of hydrochloric acid on acetaldehyde.[10]

There is, however, still a third possibility, namely, the formation of a butylene oxide ring derivative (III) obtained by ring closure due to wandering of a hydrogen atom



I III

This compound would be analogous to the *oxide ring form of a tetrose.*

It was to distinguish among these three formulas (designated below as I, II and III) that the present investigation was undertaken.

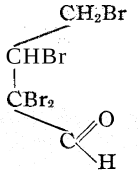
---

[7] A. Michael, "Ueber einige Gesetze und deren Anwendung in der organischen Chemie," J. *prakt. Chem.*, 60, 291 (1899).

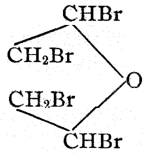
[8] Stepanov, Preobrashenski and Shchukina, ***Ber.***, **59B,** 2533 (1926).

[9] Hibbert and Hill, THIS JOURNAL, 45, 734 (1923).

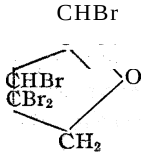
[10] Lieben, *Ann.*, 106, 336 (1858).



I



II



III

The substance (II) ($C_4H_6OBr_4$) contains two more hydrogen atoms than I and III ($C_4H_4OBr_4$). Analysis of the tetrabromo compound, prepared by Freundler's procedure, gave: C, 12.74; H, 1.60; Br, 52.2; calcd. for $C_4H_4Br_4O$: C, 12.36; H, 1.03; Br, 82.4; calcd. for $C_4H_6Br_4O$: C, 12.31; H, 1.54; Br, 82.0. The analysis thus favors the ether formula, II.

Further evidence for the ether formula, II, was obtained by condensing the compound with ethylene glycol; bromo-ethylidene glycol being obtained in 57.2% yield.

Final definite proof of the symmetrical tetrabromodiethyl ether formula II, was obtained by its direct synthesis and comparison with Freundler's compound. The product was obtained by the addition of bromine to divinyl ether, the latter being prepared by the action of powdered caustic potash on β,β'-dichloro-ethyl ether.

$$(CH_2ClCH_2)_2O + 2KOH = (CH_2{=}CH)_2O + 2KCl$$
$$(CH_2{=}CH)_2O + 2Br_2 = (CH_2BrCHBr)_2O$$

The melting points of symmetrical tetrabromo-ethyl ether prepared in this way, of Freundler's compound, and of a mixture of equal parts of the two, were found to be identical. The analyses were also in agreement, thus definitely establishing the identification of Freundler's compound as symmetrical tetrabromo-ethyl ether. It seems probable that *both* this and tetrabromobutyraldehyde are present in the reaction mixture obtained in the bromination of paracetaldehyde, but that the latter has not, as yet, been isolated.

The preparation of divinyl ether from dichloro-ethyl ether constitutes a new synthesis of this product and makes it easily available for investigation. It readily undergoes polymerization on warming, more rapidly in presence of a trace of benzoyl peroxide. These properties are being further investigated in connection with a general study on the nature of polymerization.

Experimental

Preparation of Freundler's Tetrabromo Compound.—The procedure followed was essentially that of Freundler:[3] 200 g. of bromine was added slowly from a dropping funnel to 70 g. of paracetaldehyde contained in a three-necked flask fitted with a stirrer and mercury seal and protected from moisture by a calcium chloride tube. The flask was surrounded by a freezing mixture of ice and salt and the temperature during addition was kept at −5 to −10° by adjusting the rate of addition of bromine. This required one and one-half to two hours. An additional 120 g. of bromine was then added at −5° during the course of about fifteen minutes. The temperature was allowed to rise gradually to 15°,[11] was held at this temperature for fifteen minutes, then allowed to rise to 20° and kept there until the red color of the bromine disappeared. The reaction product was then poured on a mixture of ice and finely ground sodium carbonate crystals, and the whole well stirred until all the hydrobromic acid was neutralized. The tetrabromo compound was deposited in white crystals. These were separated by filtration, dried between filter papers and recrystallized from ether; yield, 35%; m. p. 63–65".

Anal. Subs., 0.2414, 0.2040, 0.2008: CO_2, 0.1110, 0.0955, 0.0951; H_2O, 0.0370, 0.0278, 0.0298. Subs., 0.1385, 0.1017; AgBr, 0.2680, 0.1963. Calcd. for $C_4H_6Br_4O$: C, 12.31; H, 1.54; Br, 82 0. Calcd. for $C_4H_4Br_4O$: C, 12.36; H, 1.03; Br, 82.4. Found C, 12 54, 12.76, 12 91; H, 1.70, 1.51, 1.60; Br, 82.3, 82.1. Subs., 0.8415; benzene, 21.96 g ; *At*, 0.510°. Calcd. for $C_4H_6Br_4O$: mol. wt., 389.7. Found: 375.9.

Condensation with Ethylene Glycol.—One hundred and fifty-five g. of the tetrabromo compound and 300 g. of ethylene glycol were heated on the water-bath for six hours with constant stirring. The reaction mixture was extracted with ether, the ether extract first washed with saturated calcium chloride solution, then with saturated sodium bicarbonate, dried over calcium chloride and distilled under reduced pressure. The lower fractions (b. p. 65–80° at 27 mm.) still contained ethylene bromohydrin. They were redissolved in ether, the ether solution was thoroughly washed with water, dried over calcium chloride, redistilled and the distillate added to the main fraction; total yield, 75.5 g. (57.2%); b. p. 80–82° at 27 mm.

Anal. Subs., 0.1669, 0.1669, 0.1687: AgBr, 0.1867. 0.1911, 0.1909. Calcd. for $C_4H_7O_2Br$: Br, 47.83. Found: Br, 47.62, 48.28, 48.2.

Preparation of Divinyl Ether.—Two hundred grams of finely-powdered caustic potash contained in a small copper flask was strongly heated by a Bunsen burner and fifty grams of β,β'-dichloro-ethyl ether slowly dropped onto the heated alkali during the course of twelve hours. The flask was provided with a reflux water condenser kept at 40°, thus permitting the escape of the divinyl ether (b. p. 34–35°), but not of the intermediate product, vinyl chloro-ethyl ether (b. p. 106–108"). The first condenser was connected in turn to a second, and this with a well-cooled receiving flask. The refluxing was continued for about forty-eight hours; yield, 13.4 g. (54.9%); b. p. 34–35°.

Preparation of Symmetrical Tetrabromo-ethyl Ether.—One gram of divinyl ether was dissolved in 10 cc. of chloroform and a solution of 4.5 g. of bromine in 15 cc. of chloroform slowly added, the reaction flask being immersed in a freezing mixture during the addition.[12] On evaporation of the chloroform a product was left which crystallized on rubbing violently with a glass rod. It was recrystallized from ether; m. p. 63–64°. A mixture of equal parts of the compounds prepared by this, and by Freundler's method, respectively, melted at 62.5–64°.

Anal. Calcd. for $C_4H_6OBr_4$: Br, 82.03. Found: Br, 82.30, 81.75. Calcd. for $C_4H_6OBr_4$: C, 12.31; H, 1.54. Found: C, 12.68, 12.60; H, 1.77, 1.66.

Summary

1. The crystalline product obtained by Freundler in the bromination of paracetaldehyde and described by him as tetrabromobutyraldehyde is shown to be symmetrical tetrabromodiethyl ether.

---

[11] If temperature is allowed to rise too rapidly, the reaction gets beyond control and an explosion may occur.

[12] When working on a large scale it is possible to add free bromine directly to the carefully cooled divinyl ether. The reaction product is then poured onto a mixture of powdered ice and sodium carbonate as in Freundler's preparation.

2. The latter has been synthesized from divinyl ether and found to be identical with Freundler's compound.'

3. A new and simple synthesis of divinyl ether is described.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DIVISION OF RESEARCH, DEPARTMENT OF PUBLIC WORKS, BUREAU OF STANDARDS, CITY OF BALTIMORE]

EMPLOYMENT OF PYRIDINE AS CATALYST IN PRODUCTION OF DIMETHYL-ALPHA-NAPHTHYLAMINE

BY FREDERICK G. GERMUTH

RECEIVED DECEMBER 28, 1928 PUBLISHED MAY 6, 1929

Introduction

Subsequent experimentation carried on by the author with the view of ascertaining means of increasing the yield of terpineol from a-pinene and benzenesulfonic acid in acetic acid solution by inducing catalysis, developed the interesting fact that the presence of a-picoline ($NC_5H_4CH_3$) tended to increase the rate at which production occurred, accompanied by an increase in the actual yield of the product. This increase, however, is not greatly in excess of the quantity of terpineol obtained by the usual method.

It has been shown[1] that when an increase in the moisture content obtains the effect of such treatment upon the production of the substance sought is not proportional to the amount of water added at varying temperatures. It is believed that higher temperatures compensate for the decided increase in water content. The addition of α-picoline in minute and larger quantities increased the yields to an average of 2.35% in excess of those previously furnished. Unsuccessful attempts were made to enlarge this figure by the application of pyridine, (C_5H_5N), and related substances, but without avail.

It was considered advisable to test the effect of adding pyridine and certain of its homologs to reacting proportions of a-naphthylamine and methyl sulfate in alkaline solution to ascertain what effect, if any, the aromatic compound might have upon the mechanism of the reaction involved in the production of dimethyl-or-naphthylamine. The addition of a-picoline and that of the β-variety having been previously resorted to without the attainment of the sought-for objective, the contemplated step appeared feasible.

The discovery was made by the author that the yield of this methylated substitution product of naphthalene is greatly increased when the heterocyclic base is utilized as carrier. This compound has been used successfully as catalyst in Perkin's synthesis of cinnamic acid in this country[2] as well

---

[1] Germuth, *Am. J. Pharm.*, 99, 402 (1927).

[2] Bacharach and Brogan, THIS JOURNAL, SO, 3333 (1928).

as in Europe,[3] publication of the respective investigations occurring almost simultaneously. The results observed by the employment of pyridine in the role of catalyst in the production of dimethyl-a-naphthylamine form the theme considered and presented in this paper.

Method Employed.—Fourteen and three-tenth grams (0.1 mole) of α-naphthylamine was suspended in 25 cc. of water (temperature approximately 80°); to this was added 15 cc. of 40% sodium hydroxide and 25.3 g. (0.2 mole) of methyl sulfate. Each of these was added to the suspension of a-naphthylamine in water at equivalent rates, the temperature being maintained between 57 and 60°. The mixture was thoroughly stirred and the oil separated. Distillation in *vacuo* was then carried out. After this step was accomplished, about 25 g. of acetic anhydride was added. (A slight excess of the anhydride should be added until a constant temperature is maintained. The production of acetyl monomethyl-a-naphthylamine from monomethyl-α-naphthylamine present in solution is then attained.)

The mixture is poured into sufficient 28% sulfuric acid to provide for the presence of free hydrogen ions. The temperature of the acid should not be greater than 15°. This is then rendered slightly alkaline with a 28% solution of sodium hydroxide and thoroughly agitated. The separated oil is vacuum distilled. Dimethyl-α-naphthylamine passes over at 130–132° under a pressure of 8 mm. of mercury.

Purity of Materials.—The pyridine utilized in this work was of C. P. grade, possessing a boiling point of 116.5" and a specific gravity of 1.0035 at 0°. It was deemed unnecessary to attempt further purification.

The methyl sulfate employed possessed a boiling point of 188.5" and the specific gravity was 1.3278 at 20°. This compound was free from methyl sulfuric acid.

A very pure grade of α-naphthylamine was obtained by the action of sodamide upon naphthalene at a temperature of 215–220°. This substitution product possessed a specific gravity of 1.2230 at 24.8" and melted sharply at 50.2".

The sodium hydroxide was further purified and upon analysis was found to contain but a trace of carbonate.

Experimental Work

Ten portions of dimethyl-a-naphthylamine were prepared, using the method given in this paper. Table I enumerates the results observed, showing the corresponding quantities of material produced in the treated samples.

TABLE I

YIELD OF DIMETHYL-α-NAPHTHYLAMINE OBTAINED (WITHOUT PYRIDINE)

Sample no.	1	2	3	4	5	6	7	8	9	10
Actual yield, g.	9.0	8.9	8.9	8.8	9.0	8.9	8.8	8.9	8.6	8.9
% of theoretical	52.1	51.4	51.4	50.8	52.1	51.4	50.8	51.4	49.7	51.4

Average, 51.3.

It will be observed that the differences existing in percentages of yields obtained are not in excess of those usually encountered in experimental work of this nature, particularly when small amounts of materials are utilized.

---

[3] Kalnin, *Helv. Chim. Acta,* 11, 2416 (1928).

Ten additional samples were now prepared and treated precisely as those constituting the former series except that 0.1 g. of pyridine was added to the contents of each container before the addition of sodium hydroxide and methyl sulfate. The percentage yield of dimethyl-a-naphthylamine was so increased by this procedure that further experimentation, employing varying quantities of pyridine, was immediately undertaken. Continued investigation disclosed the fact that when four drops (approximately 0.2 cc.) of pyridine, equivalent to eighty drops or approximately 4 cc. of pyridine per mole of a-naphthylamine, was added to the mixture, most gratifying results were noted.

Table II shows the increased yield of dimethyl-a-naphthylamine produced by the application of pyridine to the test solutions.

TABLE II

YIELD OF DIMETHYL-α-NAPHTHYLAMINE OBTAINED

Addition of pyridine, 4 cc. per mole of a-naphthylamine

Sample no.	1	2	3	4	5	6	7	8	9	10
Actual yield, g.	11.4	11.3	11.4	11.5	11.3	11.5	11.3	11.5	11.3	11.5
% of theoretical	65.9	65.1	65.9	66.4	65.1	66.4	65.1	66.4	65.1	66.4

Average, 65.8.

In each instance the purity of the dimethyl-a-naphthylamine was determined by the usual tests (reaction, specific gravity and boiling point), and the high degree of purity of the product confirmed.

Summary

The employment of pyridine as catalytic agent in the production of dimethyl-a-naphthylamine from a-naphthylamine and methyl sulfate increases the yield of the compound from an average of 51.3% to 65.8%, when this base is utilized in the proportion of four cubic centimeters of pyridine per mole of a-naphthylamine.

Smaller quantities than that advocated do not furnish the yield attained by the amount of pyridine stipulated. Larger proportions fail to increase the quantity of dimethyl-a-naphthylamine obtained under the conditions maintained. The material produced in the presence of pyridine is of high quality.

MUNICIPAL OFFICE BUILDING
BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARSENIC TRIOXIDE

BY F. F. BLICKE AND F. D. SMITH[1,2]

RECEIVED DECEMBER 28, 1928 PUBLISHED MAY 6, 1929

This investigation is the first part of a study of certain arsenicals which we synthesized in the hope that they might be found to be of value as spirocheticides.

Tetra-arylarsyl oxides,[3] which were required for the preparation of other compounds, can be obtained quite readily by the interaction of aromatic Grignard reagents and arsenic trioxide; in addition to the oxides there are usually obtained varying amounts of triarylarsines. Hitherto there has been lack of agreement among various investigators regarding the optimum conditions for the formation of these compounds and the reaction mechanism by which they are produced.

Sachs and Kantorowicz[4] state that at a low temperature phenylmagnesium bromide and arsenic trioxide react to form tetraphenylarsyl oxide, while at a higher temperature triphenylarsine is produced. They claim, furthermore, that p-tolylmagnesium bromide and arsenic trioxide yield only tri-ptolylarsine, regardless whether the reaction is carried out at a low or high temperature.

Recently, Matsumiya and Nakai[5] found that phenylmagnesium bromide and arsenic trioxide yield invariably a mixture of tetraphenylarsyl oxide and triphenylarsine, both at low and high temperatures; similar results were obtained with p-tolylmagnesium bromide, but in the case of α-naphthylmagnesium bromide only one product seemed to be formed, a compound stated to be either $(C_{10}H_7)_4As_2O \cdot H_2O$ or $(C_{10}H_7)_2As(OH)$. Experimental evidence which we obtained indicates that neither of these formulas is correct. If the compound possessed the first of the above formulas it should react with ethylmagnesium bromide with the liberation of two molecular equivalents of ethane; a compound of the second type should yield one equivalent of the gas. It was found that no gas was evolved when the

---

[1] This paper represents the first part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] The investigation was made with the assistance of the Parke, Davis and Company Fellowship and we wish to express our appreciation for the aid which has been given us.

[3] It seems to us that the use of the term "arsyl" [Steinkopf and Smie, Ber., 59, **1456 (1926)**] permits one to apply a more rational system of nomenclature to the arsenic compounds which we have investigated than that commonly used. We have called AsH_3 and AsR_3, arsine and triarylarsine, respectively; $—AsH_2$ and $—AsR_2$, arsyl and diarylarsyl; $H_2As—O—AsH_2$ and $R_2As—O—AsR_2$, arsyl oxide and tetra-arylarsyl oxide; $H_2As—AsH_2$, diarsyl and $R_2As—AsR_2$, tetra-aryldiarsyl.

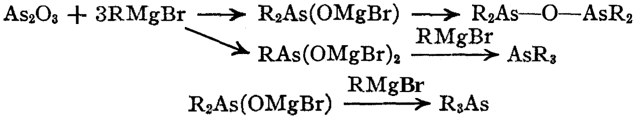
[4] Sachs and Kantorowicz, Ber., 41, **2767 (1908).**

[5] Matsumiya and Nakai, Mem. *Coll. Sci., Kyoto Imp. Univ.*, **8, 307 (1925).**

naphthyl compound was treated with ethylmagnesium bromide. Furthermore, we found the molecular weight of the substance to be 680. The naphthyl compound, therefore, seems to possess the normal structure $(C_{10}H_7)_2As\text{-}O\text{-}As(C_{10}H_7)_2$.

We have studied the action of arsenic trioxide on phenyl-, *p*-tolyl-, *p*-anisyl-, α-naphthyl- and biphenylmagnesium halides. In the case of some of the tetra-arylarsyl oxides we have greatly increased the yields obtained by other investigators by the use of procedures which are fully described in the experimental part of this paper. Tetrabiphenylarsyl oxide has not been prepared hitherto. With the first three Grignard reagents mentioned above, mixtures of tetra-arylarsyl oxides and triarylarsines were obtained, regardless of the way in which the experimental conditions were varied, but with the last two arylmagnesium halides only tetra-arylarsyl oxides were found to be formed.

Concerning the manner in which the tetra-arylarsyl oxides and the triarylarsines are produced, Sachs and Kantorowicz suggested the following scheme but gave no experimental evidence in support of their view.



$$As_2O_3 + 3RMgBr \longrightarrow R_2As(OMgBr) \longrightarrow R_2As\text{—}O\text{—}AsR_2$$

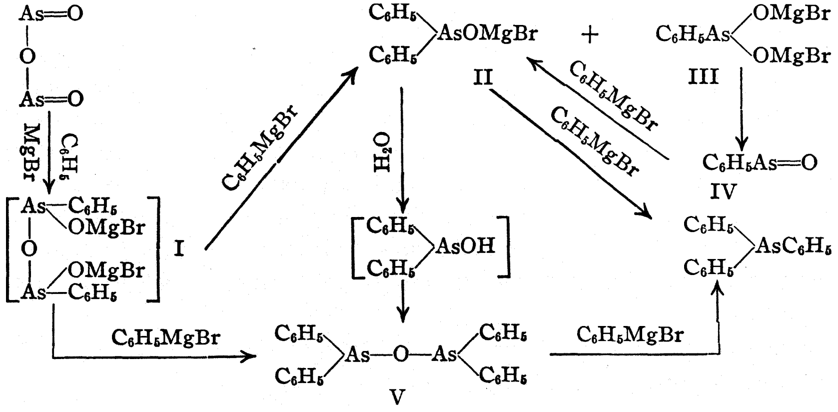
$$3RMgBr \searrow RAs(OMgBr)_2 \xrightarrow{RMgBr} AsR_3$$

$$R_2As(OMgBr) \xrightarrow{RMgBr} R_3As$$

Matsumiya and Nakai, as well as Gryszkiewicz-Trochimowski and Zambrzycki,[6] who studied the action of phenylmagnesium bromide on arsenic trioxide, considered it probable that the reaction proceeded in the following stages.

$$As_2O_3 \xrightarrow{4RMgBr} R_2As\text{—}O\text{—}AsR_2 \xrightarrow{2RMgBr} 2R_3As$$

A consideration of the various possible reactions which might take place when a Grignard reagent, phenylmagnesium bromide for example, reacts with arsenic trioxide leads to the following formulation.



---

[6] Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemij*, 6, 798 (1926).

One of the first questions which arises in connection with the study of the mechanism of the reaction is this: Is tetraphenylarsyl oxide, V, formed directly from the inorganic oxide (possibly through intermediate formation of I) or is it produced from Compound II by the addition of water to the reaction mixture?

When phenylmagnesium bromide reacts with arsenic trioxide, in the presence of a mixture of ether and benzene, a heavy precipitate soon forms. After completion of the reaction and the removal of most of the ether, the precipitate was separated from the solvent and decomposed with water. Four-fifths of the total amount of tetraphenylarsyl oxide formed was obtained from the precipitate, while the remainder of the arsyl oxide and triphenylarsine was isolated from the benzene layer. If tetraphenylarsyl oxide had been formed directly from arsenic trioxide, and hence were present as such in the reaction mixture, it seems that all of the tetraphenylarsyl oxide should have been obtained from the benzene layer and none from the precipitate;[7] more than enough solvent was employed to hold in solution all of the tetraphenylarsyl oxide which could possibly have been formed from the amount of arsenic trioxide used.

It seems to us that the above phenomena may be accounted for if the assumption is made that $(C_6H_5)_2As\text{-}OMgBr$, a substance which might be expected to be only slightly soluble in benzene, is the precursor of tetraphenylarsyl oxide and that the latter compound is produced only after the addition of water to the precipitate mentioned above.

The same type of phenomenon was encountered in the case of α-naphthyl- and biphenylmagnesium bromide except that in the latter instance all of the tetra-aryl oxide was obtained from the precipitate after decomposition of the latter with water. No precipitates, however, were formed with the tolyl- and anisylmagnesium halides. We can only suggest that in these instances the compounds of the type $R_2As\text{-}OMgX$ may be more soluble.

Compound IV, which would probably be produced by spontaneous decomposition of III, could not be found among the reaction products from phenylmagnesium bromide and arsenic trioxide. We have shown that this substance reacts with phenylmagnesium bromide to form either a mixture of tetraphenylarsyl oxide and triphenylarsine or is converted quantitatively into triphenylarsine, depending on experimental conditions. It was found, also, that tetraphenylarsyl oxide, under proper conditions, reacts with phenylmagnesium bromide to form triphenylarsine in quantitative yield.

Finally, we prepared a number of diarylarsyl halides, some of which have not been described previously.

---

[7] This consisted, in part, of inorganic magnesium salts.

Experimental Part

Aromatic Grignard Reagents and Arsenic **Trioxide**[8,9] **Phenylmagnesium** Bromide.—The reagent was prepared from 62.8 g. of bromobenzene (0.4 mole), 9.7 g. of magnesium (0.4 mole) and 200 cc. of ether in a liter, three-necked flask, fitted with a reflux condenser and then diluted with an equal volume of benzene. The flask was cooled in an ice-bath and a mechanical stirrer introduced. In this experiment, as well as in all of the following ones, moisture was prevented from entering the apparatus. Nineteen and eight-tenths g. (0.1 mole) of dry arsenic trioxide was added as rapidly as possible while the mixture was stirred vigorously. It was found that rapid addition of the arsenic trioxide to the thoroughly cooled reaction mixture reduced the amount of triphenylarsine to a minimum. After all of the oxide had been added, the ice-bath was removed. A colorless precipitate, probably $(C_6H_5)_2AsOMgBr$ and inorganic magnesium salts, soon formed with the evolution of considerable heat.

After the mixture had been stirred for four hours, the solvent was removed under diminished pressure, in a stream of dry nitrogen, until the reaction mixture was reduced to about one-third of its original volume. When the solid material had settled, the benzene layer was decanted and the former substance was decomposed with ice and a small amount of acetic acid. The organic material was extracted with benzene, the benzene solution was shaken with dilute aqueous sodium hydroxide and then dried with fused sodium sulfate. The solvent was removed on a steam-bath and the oily residue allowed to solidify. The material was washed thoroughly with petroleum ether (40–60°) and then with a mixture of ether and petroleum ether; m. p. 92.5–93.5°. This substance was pure tetraphenylarsyl oxide. The yield was 21 g.

The solvents with which the tetraphenylarsyl oxide had been washed were now added to the benzene layer mentioned above and the mixture was treated with ice and a small amount of acetic acid. After separation of the benzene layer, the latter was washed with dilute sodium hydroxide solution, dried and the solvent removed. The oily residue solidified to an amorphous mass. After the latter had been treated with petroleum ether several times, it melted at 91–92° and hence was tetraphenylarsyl oxide; yield, 5 g. The total yield of this oxide was 26 g., or 55% of the calculated amount. The petroleum ether with which the above material had been washed was concentrated to a very small volume and then diluted with 25 cc. of dry ether. Upon the addition of mercuric chloride dissolved in ether the mercuric chloride addition product of triphenylarsine was precipitated. The latter weighed 10.2 g. and corresponds to 5.4 g. of triphenylarsine.

The following experiment shows that triphenylarsine is precipitated practically quantitatively by mercuric chloride: 6.12 g. of pure triphenylarsine was dissolved in a small amount of absolute ether. Upon the addition of 5.42 g. of dry mercuric chloride, dissolved in 250 cc. of ether, a precipitate was obtained which weighed 11.30 *g.;* calcd. weight of addition product, 11.54 g. Triphenylarsine can be obtained from the addition product if the latter is suspended in alcohol and then treated with hydrogen sulfide.

---

[8] Very little information is to be found in the literature regarding the action of aliphatic Grignard reagents on arsenic trioxide. Sachs and Kantorowicz, Ber., 41, 2769 (1908), state that iso-amylmagnesium bromide reacts with arsenic trioxide with the formation of an oil. Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemij*, 6, 749 (1926), studied the action of methyl-, ethyl-, propyl- and allylmagnesium halides on arsenic trioxide and were able to isolate only trialkylarsines in rather poor yields.

[9] Recently, Matsumiya and Nakai, Mem. *Coll. Sci.*, Kyoto Imp. Univ., 10, 57 (1927), published their results on the action of arylmagnesium halides on arsenic trisulfide. They obtained triarylarsines and varying amounts of tetra-arylarsyl sulfides.

In one experiment an attempt was made to account for all of the material used. From 19.8 g. of arsenic trioxide and 62.8 g. of bromobenzene there were obtained 29 g. of tetraphenylarsyl oxide (equivalent to 12.1 g. of arsenic trioxide and 38.4 g. of bromobenzene), 10.2 g. of the mercuric chloride addition product of triphenylarsine (equivalent to 1.7 g. of arsenic trioxide and 8.3 g. of bromobenzene), 3.5 g. of biphenyl (equivalent to 7.1 g. of bromobenzene), 5.4 g. of unchanged arsenic trioxide and a small amount of phenol. The total amount of bromobenzene thus accounted for is 53.8 g., or 85.5% of that used; the amount of arsenic trioxide, 19.3 g., or 97% of that employed.

After conversion of the oxide into diphenylarsyl chloride, purification of the latter by distillation and hydrolysis of the chloride into the original oxide, the latter was recrystallized from alcohol; m. p. 95.5–96.5°. The highest melting point recorded previously was 92.5–93.5°.[10]

p-Tolylmagnesium Bromide.—After 68.4 g. of p-bromotoluene and 9.7 g. of magnesium in 200 cc. of ether had reacted completely, the solution was diluted with 200 cc. of dry benzene. The contents of the flask were then cooled, stirred vigorously and 19.8 g. of dry arsenic trioxide was added as quickly as possible. In this instance no precipitate formed. The mixture was stirred for four hours and then decomposed with ice and a small amount of acetic acid. The ether–benzene layer was separated, washed with dilute sodium hydroxide solution and then dried with fused sodium sulfate. The solvent was removed and the oily residue dissolved in absolute ether. The ether solution was treated with mercuric chloride dissolved in ether until a precipitate no longer formed. The precipitate, which was the mercuric chloride addition product of tritolylarsine, was removed by filtration. The filtrate was shaken with dilute hydrochloric acid to remove mercuric chloride, dried and the solvent removed. The solid residue was washed thoroughly with petroleum ether (40–60°). The yield of tetra-p-tolylarsyl oxide was 25.5 g., or 48% of the calculated amount. After recrystallization from alcohol the compound melted at 108.5–109.5°. The amount of tritolylarsine formed, calculated on the basis of the addition product, was 9 g.

Sachs and Kantorowicz[4] obtained only tritolylarsine but no arsyl oxide from p-tolylmagnesium bromide and arsenic trioxide. From the interaction of the two latter substances Matsumiya and Nakai[11] obtained a 10% yield of tetratolylarsyl oxide and recorded the melting point as 105–106°.

p-Anisylmagnesium Iodide.—The Grignard reagent was prepared from 93.6 g. of p-iodo-anisole,[12] 9.7 g. of magnesium and 250 cc. of ether. Two hundred and fifty cc. of dry benzene was then added; the subsequent procedure was the same as that described above for p-tolylmagnesium bromide.

There was obtained 33 g. of tetra-p-anisylarsyl oxide; m. p. 127–129°. This corresponds to a yield of 56%. In addition, 12 g. of trianisylarsine was formed.

Tetra-p-anisylarsyl oxide had been obtained previously by Michaelis and Weitz,[13] by the action of hydriodic acid on tri-p-anisylarsine and subsequent hydrolysis of the dianisylarsyl iodide. The substance obtained by them melted at 130°.

α-Naphthylmagnesium Bromide.—This reagent was prepared from 91 g. of pure α-bromonaphthalene[14] (0.44 mole), 9.7 g. of magnesium (0.40 mole) and 200 cc. of ether. An equal volume of benzene was then added to prevent the separation of solid naphthylmagnesium bromide from the solution. The mixture was stirred vigorously and 19.8 g. (0.10 mole) of arsenic trioxide was added. During the latter operation no external

---

[10] McKenzie and Wood, *J. Chem. Soc.*, **117**, 412 (1920).

[11] Matsumiya and Nakai, Mem. *Coll. Sci., Kyoto* Imp. *Univ.*, *8*, 312 (1925).

[12] Blicke and Smith, THIS JOURNAL, **50**, 1229 (1928).

[13] Michaelis and Weitz, *Ber.*, **20**, 50 (1887).

[14] Blicke, THIS JOURNAL, 49, 2846 (1927).

cooling was necessary. After some time a heavy precipitate formed. The mixture was stirred for four hours and then ice and a small quantity of acetic acid were added. The mixture was shaken vigorously and after a short time two distinct layers formed rather suddenly. The ether–benzene layer was then decanted immediately. Within a few minutes tetra-α-naphthylarsyl oxide began to separate, and was completely precipitated after a few hours. The organic oxide was filtered and air-dried. The material was recrystallized from tetralin, suspended in hot benzene to remove any tetralin and filtered; m. p. 250–253° with decomposition. The yields of crude tetranaphthylarsyl oxide averaged 52 g., which corresponds to 77% of the calculated amount. No trinaphthylarsine could be discovered among the reaction products. From α-bromonaphthalene and arsenic trioxide Matsumiya and Nakai[15] obtained a 32% yield of the arsyl oxide. They found the melting point of the substance to be 240–241°.

p-Bromobiphenylmagnesium Bromide.—The Grignard compound was prepared from 31 g. of *p*-bromobiphenyl,[16] 4.0 g. of magnesium and 200 cc. of ether in a *500-cc.* round-bottomed flask which had been modified in the following manner. A glass tube 1 cm. wide and about 15 cm. long was sealed to the body of the flask a short distance from the neck of the latter. About 3 cm. beyond the point of attachment the glass side arm was bent at a right angle toward the bulb of the flask. During the preparation of the Grignard reagent the arm of the flask was closed with a cork. After the above mixture had been heated for about ten hours, the solution of the Grignard reagent was decanted through the side arm from unchanged magnesium and dibiphenyl into a liter 3-necked flask which had been fitted with a reflux condenser and a mechanical stirrer. Two hundred cc. of dry benzene and 100 cc. of ether were added to the mixture and the latter was cooled and stirred vigorously. Upon addition of the arsenic trioxide (6.6 g.) a vigorous reaction took place. A precipitate soon formed which coated the surface of the unchanged inorganic oxide. The reaction mixture was stirred for four hours and the precipitate was then allowed to settle. After twelve hours the liquid layer was decanted[17] and the solid material decomposed as usual. The organic matter was extracted with benzene; the benzene solution was dried and filtered. After removal of the solvent 10 g. of crude tetrabiphenylarsyl oxide was obtained; this yield corresponds to 39% of the calculated amount. The crude material melted about 132–138°. After conversion of the oxide into the chloride, recrystallization of the latter and hydrolysis into the tetra-arylarsyl oxide, the substance melted at 150–152°.

From the experiments described below it can be seen that in the interaction of phenylmagnesium bromide with phenylarsyl oxide, $(C_6H_5)As{=}O$ (or with $(C_6H_5)_2As\text{-}OMgBr$), a large excess of the arylmagnesium halide favors the formation of triphenylarsine to a very decided extent. In the first instance there was used twice the amount of phenylmagnesium bromide necessary for the formation of the arsine; in the second instance eight times the calculated amount of Grignard reagent.

Phenylmagnesium Bromide **and Phenylarsine** Oxide.—Presumably these two compounds react first in accordance with the following

$$C_6H_5MgBr + C_6H_5As{=}O \longrightarrow (C_6H_5)_2As\text{—}OMgBr$$

The diaryl compound then reacts with the Grignard reagent to form the tertiary arsine.

---

[15] Matsumiya and Nakai, Mem. *Coll. Sci.*, Kyoto Imp. *Univ.*, 8, 313 (1925).

[16] Gomberg and Bachmann, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 42.

[17] Upon evaporation of the solvent only biphenyl was obtained.

1. phenylmagnesium bromide was formed from 5.7 g. of bromobenzene (0.037 mole), 0.9 g. of magnesium and 25 cc. of ether. After the addition of 2.7 g. of phenylarsine oxide (0.016 mole), dissolved in 25 cc. of benzene, the mixture was refluxed for three hours. There was obtained 3.0 g. of tetraphenylarsyl oxide and 0.5 g. of triphenylarsine.

2. The Grignard reagent was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Four and two-tenths g. of phenylarsine oxide (0.025 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. No tetraphenylarsyl oxide was formed. The yield of triphenylarsine was 7.4 g., or 97% of the calculated amount.

The following experiments show that triphenylarsine is produced by interaction of phenylmagnesium bromide with tetraphenylarsyl oxide. Inasmuch as the Grignard reagent and the arsyl oxide react readily even at 0° to form the arsine, it seems impossible to prevent the formation of the latter substance in the preparation of the tetra-arylarsyl oxide.

Phenylmagnesium Bromide and Tetraphenylarsyl Oxide.—The Grignard reagent was prepared from 7.3 g. of bromobenzene (0.05 mole), 0.8 g. of magnesium and 30 cc. of ether. The solution was cooled to 0° and 4.7 g. of tetraphenylarsyl oxide (0.01 mole) was added. After the mixture had remained at 0° for four hours, a heavy crystalline precipitate had formed. The ether layer was decanted from the crystalline deposit and decomposed with ice and ammonium chloride. The ether solution was dried with fused sodium sulfate and the triphenylarsine was precipitated by means of mercuric chloride. The mercuric chloride addition product was removed by filtration and the filtrate was shaken with dilute hydrochloric acid to remove excess mercuric chloride. The ether solution was dried again and the solvent removed. The pasty residue was washed with low-boiling petroleum ether to remove biphenyl. The product which remained was tetraphenylarsyl oxide. The crystalline deposit was decomposed with ice and ammonium chloride and after the addition of a small amount of ether to dissolve the material the solution was treated as described above. Tetraphenylarsyl oxide and triphenylarsine were obtained. The total yield of oxide was 2.6 g.; that of arsine was 2.1 g.

In a second experiment the reaction mixture was kept somewhat above 35°. Phenylmagnesium bromide was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Eleven and eight-tenths g. of tetraphenylarsyl oxide (0.04 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. The yield of triphenylarsine was 14.2 g.; the calculated amount is 15.3 g.

Finally, we found that arsenic trioxide and an excess of phenylmagnesium bromide react quantitatively to form triphenylarsine. Five g. of arsenic trioxide (0.025 mole) and the Grignard reagent (0.4 mole) obtained from 62.8 g. of bromobenzene, 9.7 g. of magnesium and 200 cc. of ether were refluxed for four hours. There was obtained 15.0 g. of triphenylarsine; the calculated amount of triphenylarsine is 15.2 g.

TABLE I

DIARYLARSYL HALIDES

	M. p., °C.	Formula	Analysis (Volhard) Calcd.	Analysis (Volhard) Found
1 Diphenylarsyl chloride	40–42[a]		....	......
2 Diphenylarsyl bromide	52–54[b]		....	......
3 Diphenylarsyl iodide	42–43[c]		....	......
4 Di-*p*-tolylarsyl chloride	44–45[d]		....	......
5 Di-p-tolylarsyl bromide	65–66	$C_{14}H_{14}AsBr$	Br, 23.73	23.65, 23.70

TABLE I (*Concluded*)

	M. p., °C.	**Formula**	**Analysis (Volhard)** Calcd.		**Found**
6 Di-p-tolylarsyl iodide	64–65	$C_{14}H_{14}AsI$	I,	33.07	33.10, 33.02
7 Di-p-anisylarsyl chloride	83–84[e]		....		....
8 Di-*p*-anisylarsyl bromide	60–62	$C_{14}H_{14}O_2AsBr$	Br,	21.68	21.20, 21.22
9 Di-*p*-anisylarsyl iodide	40–42[f]	$C_{14}H_{14}O_2AsI$	I,	30.52	30.60, 30.43
10 Di-p-naphthylarsyl chloride	167–168[g]		....		....
11 Di-*p*-naphthylarsyl bromide	172–173	$C_{20}H_{14}AsBr$	Br,	19.56	19.45, 19.41
12 Di-p-naphthylarsyl iodide	140–141	$C_{20}H_{14}AsI$	I,	27.85	27.65, 27.70
13 Dibiphenylarsyl chloride	145–147	$C_{24}H_{18}AsCl$	Cl,	8.52	8.48, 8.45
14 Dibiphenylarsyl bromide	147–149	$C_{24}H_{18}AsBr$	Br,	17.35	17.54, 17.23
15 Dibiphenylarsyl iodide	140–141	$C_{24}H_{18}AsI$	I,	25.00	24.73, 24.80

The chlorides were prepared from the tetra-arylarsyl oxides and hydrogen chloride; the bromides from the oxides and hot 48% hydrobromic acid; the iodides from the chlorides and sodium iodide in acetone.

Compounds 1, 2, 3, 4, 5, 6, 7, 8 and 9 were recrystallized from absolute alcohol; 10, 11, 12, 13 and 15 from benzene; 14 from a mixture of benzene and absolute alcohol.

[a] The m. p. recorded by Norris, *J. Ind. Eng. Chem.*, 11, 824 (1919), is 34°.

[b] Michaelis and La Costa, *Ann.*, 201, 230 (1880), described the compound as an oil; Pope and Turner, *J. Chem. Soc.*, 117, 1452 (1920), give the m. p. as 55–56°; Steinkopf and Schwen, *Ber.*, 54, 1459 (1921), record the m. p. as 54°.

[c] The m. p. given by Pope and Turner[b] is 45–46°; Steinkopf and Schwen[b] state the m. p. to be 40.5°.

[d] La Costa, *Ann.*, 208, 18 (1881), recorded the m. p. as 31°; Michaelis, *Ann.*, 321, 160 (1902), as 45°.

[e] Michaelis and Weitz, *Ber.*, 20, 50 (1887), found the m. p. to be 79–80°.

[f] Michaelis and Weitz[e] obtained the substance as an oil.

[g] Matsumiya, *Mem. Coll. Sci., Kyoto Imp. Univ.*, 4, 217 (1920).

Summary

A reaction mechanism has been suggested to account for the products which are formed from the interaction of aromatic Grignard reagents and arsenic trioxide.

Improved methods have been described for the preparation of tetraphenyl-, tetra-p-tolyl-, tetra-p-anisyl- and tetra-α-naphthylarsyl oxides. Tetra-p-biphenylarsyl oxide has been synthesized.

A number of diarylhalo-arsines have been prepared and described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE ACTION OF SULFUR ON NORMAL-HEPTANE AND NORMAL-BUTANE

BY R. B. BAKER[1] AND E. EMMET REID

RECEIVED JANUARY 11, 1929 PUBLISHED MAY 6, 1929

Introduction

The action of sulfur on organic compounds has been the subject of many investigations.[2] Friedmann[3] investigated the action of sulfur on n-octane when heated under pressure. He obtained a thiophene, $C_8H_{12}S$, and a thiophthene compound, $C_8H_8S_2$.

The Present Investigation

n-Heptane and n-butane were heated with sulfur. The results obtained, so far as they go, are analogous to those of Friedmann. Heptane gives a substituted thiophene and n-butane seems to give thiophene itself, though the yields from both hydrocarbons were very small.

Experimental

***n*-Heptane.** Sealed Pyrex Tubes.—Three g. of sulfur and 11 g. of heptane were heated in each tube at temperatures varying from 150 to 250° for periods of four to twenty-four hours. On cooling the tubes were placed in "dry ice" before opening. The liquid was fractionated and consisted mostly of unchanged heptane. A very small residue boiling above 100° was obtained.

Steel Bombs.—Much larger amounts of materials were used in the bombs, which were heated to temperatures of 300–350° for periods of twenty-four to forty-eight hours. A charge consisted of 12.8 g. of sulfur and 40 g. of heptane. The residues from the bombs, after distilling off the unchanged heptane, were not much greater in proportion than those obtained from the glass tubes. There is very little indication of reaction under these conditions. However, the various residues were combined and fractionated. A fraction (about 2 g.) boiling at 160–161° was collected. A few drops of this liquid when treated with alcoholic mercuric chloride gave a pale yellow precipitate (test for thiophenes). Reasoning from the results of Friedmann's work on n-octane, heptane should give a thiophene of the empirical formula $C_7H_{10}S$. A Parr bomb determination of sulfur gave the result: calcd. for $C_7H_{10}S$: S, 25.40; found: S, 24.89, 25.04 The density was $d_{4^\circ}^{0^\circ} = 0.9332$; $d_{4^\circ}^{25^\circ} = 0.9221$.

This liquid gave positive tests for thiophenes by the methods of Fletcher and Hopkins,[4] Bauer[5] (indophenin reaction), Laubenheimer[6] and Steensma.[7] Negative tests were obtained when the liquid was examined for mercaptans[8] and sulfides.[9]

---

[1] From a part of the Ph.D. dissertation of R. B. Baker, 1928.

[2] See, for example, Steinkopf and Kirchoff, British patent 16,810, July 18, 1912; Capelle, Bull. *soc. chim.*, [4] **3**, 150 (1908); W. Friedmann, *Ber.*, **49**, 1551 (1916).

[3] Friedmann, *Ber.*, **49**, 1344 (1916).

[4] Fletcher and Hopkins, *Chem. Zentr.*, I, 1442 (1907).

[5] Bauer, *Ber.*, 37, 1244, 3128 (1904).

[6] Laubenheimer, *ibid.*, 8, 224 (1875).

[7] Steensma, *Chem. Zentr.*, I, 1492 (1908).

[8] Reid, Mackall and Miller, THIS JOURNAL, 43, 2104 (1921).

[9] Steinkopf, *Ann.*, **403**, 1 (1914).

Considerable solid matter was left in the tubes after the removal of the liquid. This proved to be sulfur mixed with some carbon.

n-Butane.—Steel bombs were used with butane and sulfur, the charge being 32 g. of butane and 15 g. of sulfur. As butane is a gas at ordinary temperatures the bomb was first well cooled in an ice-salt mixture before adding the hydrocarbon. The charge was heated for twenty-one hours at 335°.

On opening the bomb (after again cooling in ice water), a considerable amount of hydrogen sulfide was given off and the unreacted butane was volatilized. The gas evolved smelled like a low-boiling gasoline high in sulfur content. Upon opening the bomb very little residue was left (less than 1 g.). This was taken up in ether, and gave all of the above-mentioned color tests for thiophene.

Conclusions

The results obtained are analogous to those obtained by Friedmann on octane. From heptane and sulfur a thiophene and sulfur of the formula $C_7H_{10}S$ is formed in small amounts.

Similar results were obtained with butane and sulfur.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE CLAISEN ESTER CONDENSATION WITH ETHYL THIOLACETATE[1]

BY R. B. BAKER[2] AND E. EMMET REID

RECEIVED JANUARY 11, 1929 PUBLISHED MAY 6, 1929

Introduction

This investigation was undertaken with the idea in mind of comparing ethyl thiolacetate with ethyl acetate in the ordinary Claisen condensation. No sulfur esters have ever been subjected to such a reaction, and it appeared of interest to compare the products obtained with those resulting from the condensation of ethyl acetate with itself, and of ethyl acetate with a ketone and a nitrile.

Ethyl thiolacetate, $CH_3COSC_2H_5$, in the presence of sodium metal condenses in a manner quite similar to ethyl acetate, and forms a sulfur analog of acetoacetic ester, $CH_3COCH_2COSC_2H_5$. The yield of ester is rather low, being about 15% of the theoretical (calculated on the amount of ethyl thiolacetate used).

At ordinary temperatures ethyl acetothiolacetate contains about 31% of enol (determined by the bromo-titration method of Kurt Meyer),[3] as compared to about 7% in acetoacetic ester.

---

[1] Presented at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] From a part of the Ph.D. dissertation of R. B. Baker, 1928.

[3] Kurt Meyer, Ber., 44, 2718 (1911).

Acetothiolacetic ester forms metallic salts as does acetoacetic ester,[4] but the copper salt is the only one found that is stable. The others that were prepared decompose on short standing with the formation of metallic sulfides.

The conditions of hydrolysis of this ester are the same as those for acetoacetic ester. With dilute alkalies acetone is formed, and in the presence of concentrated alkalies, two molecules of acetic acid are liberated.

Like acetoacetic ester[5] the new ester decomposes on heating, but much more readily, with the formation of dehydracetic acid, $C_8H_8O_4$.

An equal molar mixture of ethyl thiolacetate and ethyl acetate condenses in the presence of sodium, and a liquid is obtained having a composition of 98% of acetothiolacetic ester (by analysis for sulfur) and 2% of acetoacetic ester. This would show that ethyl thiolacetate is more reactive than ethyl acetate in this condensation.

The Claisen condensation also takes place between an ester and a ketone. Ehrhardt and Claisen[6] prepared acetylacetone, $CH_3COCH_2COCH_3$, by condensing ethyl acetate with acetone. In attempting the same reaction with ethyl thiolacetate and acetone, however, no acetylacetone is formed but only acetothiolacetic ester. The acetone apparently has no effect upon the ethyl thiolacetate, which merely condenses with itself.

Ethyl thiolacetate condenses with acetonitrile with the formation of cyanacetone, CH_3COCH_2CN, the yield amounting to 7%. This same compound is obtained from ethyl acetate and acetonitrile with the same yield.

Experimental

Ethyl Thiolacetate.—This ester was prepared by a modification of the method of **Michler.**[7] The calculated amount of acetyl chloride was added slowly from a dropping funnel through a reflux condenser to slightly more than the calculated amount of ethyl mercaptan, contained in a flask packed in ice. After the addition of the acetyl chloride, the dropping funnel was replaced by a piece of glass tubing leading to a flask containing water to absorb the hydrogen chloride and recover any mercaptan carried over. The mixture was kept at room temperature for several days and then heated under reflux. The product was poured into water. The upper layer was separated and was washed free of acids and dried over calcium chloride. It was then subjected to fractional distillation and the portion boiling at 116–117° collected; yield, 80% of theoretical. The following physical properties were obtained: $d_{4°}^{0°} = 1.0008$; $d_{4°}^{25°} = 0.9755$; $n_D^{28°} = 1.4503$; mol. refr. $[(n^2-1)/(n^2+2)]M/d = 19.31$. Michler gives the boiling point as 114–116°. There are no data on the other properties in the literature.

Ethyl Acetothiolacetate, $CH_3COCH_2COCS_2H_5$

Preparation.—To 17 g. of sodium wire contained in a large balloon flask, 200 g. of ethyl thiolacetate was added slowly, in portions, through a reflux condenser. The top

---

[4] Conrad, *Ann.*, **188**, 269 (1877); Wislicenus, *Ber.*, 31, 3153 (1898); Lippmann, *Z. fur Chemie*, 12, 29 (1869).

[5] See Geuther, *Z. fur Chemie*, 8 (1866).

[6] Ehrhardt and Claisen, *Ber.*, 22, 1011 (1889).

[7] Michler, *Ann.*, 176, 182 (1875).

of the flask was packed with ice, as in a Grignard reaction, while the bottom was heated gradually on the water-bath to 50°. After six hours the sodium had all reacted and a yellowish pasty mass was obtained. After cooling, 50% acetic acid was added to an acid reaction. An equal volume of cold saturated sodium chloride solution was then added, the top layer separated and dried over calcium chloride. The liquid was fractionated at 2 mm. pressure in apparatus similar to that of Martin[8] as modified by Rice and Sullivan.[9] The distillate going over up to 60° bath temperature was discarded. At 60° and 2 mm. 22 g. (15% yield) of ethyl acetothiolacetate was collected. Sulfur was determined by the Parr bomb method, the liquid being introduced in small, thin-walled bulbs.

Anal. Calcd. for $C_6H_{10}O_2S$: S, 21.93. Found: S, 22.04, 21.86, 22.08.

Properties.—Ethyl acetothiolacetate is a colorless liquid with a rather disagreeable odor, having the following physical properties: $d_{4°}^{0°} = 1.0917$; $d_{4°}^{25°} = 1.0684$; $n_D^{25°} = 1.4885$; mol. refr. $[(n^2-1)/(n^2+2)]M/d = 39.46$. It is insoluble in water but dissolves in ether and alcohol in all proportions. It gives a deep red color with ferric chloride solution (presence of enol form) as does acetoacetic ester. It forms a white crystalline compound with sodium bisulfite.

Percentage of Enol Form.—A determination of the enol content of the ester by Kurt Meyer's bromo-titration method gave a mean value of 30.8%.

Metallic Salts: Copper Salt.—This salt was prepared by adding the calculated amount of a 6% solution of copper acetate to the ester diluted with 2 parts of ether. The bright green precipitate was filtered off, washed with water, then with alcohol and dried in a vacuum desiccator over sulfuric acid. The very fine crystals were found to be insoluble in water and only fairly soluble in benzene, alcohol, ether, chloroform and carbon tetrachloride, both in the hot and in the cold. The crystals decompose on heating at 110°. Copper was determined by the potassium iodide method after decomposing the organic salt in concentrated sulfuric and nitric acids. Sulfur was determined by the Parr bomb method.

Anal. Calcd. for $Cu(C_6H_9O_2S)_2$: Cu, 17.97; S, 18.12. Found: Cu, 18.12, 18.09; S, 18.01, 18.10.

Hydrolysis of Acetothiolacetic Ester

Ketone Hydrolysis.—Acetone is formed from the ester by refluxing with dilute alkali. For this purpose, 1 g. of the ester and 10 cc. of a 5% sodium hydroxide solution were refluxed for two hours in a boiling water-bath. Some of the liquid was then distilled off and acetone identified in the distillate by Gunning's method,[10] which is a modification of Lieben's iodoform test for acetone applicable in the presence of alcohol. A considerable amount of iodoform was obtained.

Acid Hydrolysis.—Acetic acid is obtained by refluxing the ester with concentrated alkali. To a solution of 3.5 g. of potassium hydroxide in 3 cc. of water, 2 g. of the ester was added. After heating in the boiling water-bath for several hours the liquid was acidified with sulfuric acid. The clear liquid was poured off from some potassium sulfate and distilled. Acetic acid was detected by the addition of absolute alcohol followed by concentrated sulfuric acid.

Decomposition of Ethyl Acetothiolacetate.—The residue from a vacuum distillation of the ester solidified on cooling. This solid was found to be very soluble in hot alcohol but insoluble in cold. After several crystallizations from alcohol, pale straw-colored

---

[8] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

[9] Rice and Sullivan, THIS JOURNAL, 50, 3048 (1928).

[10] Gunning, *Z. anal. Chem.*, **24**, 147 (1885).

needles were obtained, having a melting point of 109°. They were identified by melting point and molecular weight determinations as dehydracetic acid, $C_8H_8O_4$, a compound described by Geuther.[5]

Ethyl Thiolacetate and Ethyl Acetate.—A mixture of 50 g. of ethyl acetate and 59 g. of ethyl thiolacetate was added to 10 g. of sodium wire. After the metal had reacted, the product was worked up as above. The fraction coming over from 40–60° at 2 mm. (the boiling points of acetoacetic ester and acetothiolacetic ester, respectively) was collected. A Parr bomb analysis for sulfur gave 21.49%. As the theoretical value is 21.93%, this indicates 98% of ethyl acetothiolacetate. As a further check on this figure, the density of this liquid was taken at 25° and the value $d_4^{25} = 1.0657$ obtained.

From density measurements (at 25°) of a series of mixtures of the two esters (of known composition) a curve is obtained by plotting density against composition. The value of $d_4^{25} = 1.0657$ corresponds to a composition of 95% $CH_3COCH_2COSC_2H_5$, which agrees fairly well with the composition obtained by actual analysis.

Ethyl Thiolacetate and Acetone.—The method of Ehrhardt and Claisen[6] for the preparation of acetylacetone from ethyl acetate and acetone was used with the sulfur ester in the hope of forming the same compound but only ethyl acetothiolacetate was obtained. Apparently the acetone does not take part in the reaction, and the sulfur ester simply condenses with itself.

Ethyl Thiolacetate and Acetonitrile.—A cold mixture of 38 g. of the ester and 14 g. of acetonitrile was added to 5 g. of sodium wire. After the reaction was complete, the solid was put carefully into ice water, the lower alkaline layer separated and acidified with dilute hydrochloric acid. This was extracted several times with ether, the extract separated, and dried over calcium chloride. The ether was distilled off, and the residue fractionated. The portion boiling from 120–125° was collected. The yield of cyanacetone was 7% of the acetonitrile used.

Summary

1. Ethyl thiolacetate condenses in the presence of sodium to form a sulfur analog of acetoacetic ester, $CH_3COCH_2COSC_2H_5$.

2. The mean value of the enol content of the sulfur ester, as determined by the bromo-titration method, is 30.8% at ordinary temperatures.

'3. Acetothiolacetic ester forms metallic salts as does acetoacetic ester, but of those made only the copper salt, $C_{12}H_{18}O_4S_2Cu$, is stable.

4. Ethyl acetothiolacetate shows the ketone and acid hydrolysis, as does ethyl acetoacetate.

5. Upon heating, ethyl acetothiolacetate decomposes to form dehydracetic acid, $C_8H_8O_4$ as does ethyl acetoacetate.

6. An equal molar mixture of ethyl thiolacetate and ethyl acetate condenses with sodium to form 98% acetothiolacetatic ester and 2% acetoacetic ester.

7. Ethyl thiolacetate and acetone do not condense with sodium to form acetylacetone as would be expected; ethyl acetothiolacetate alone is produced.

8. Ethyl thiolacetate and acetonitrile condense with sodium to form cyanacetone.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF DI-PARA-TOLYL INCIDENTAL TO THE PREPARATION OF BENZYLMAGNESIUM CHLORIDE. THE PROBABLE PRELIMINARY FORMATION OF FREE RADICALS IN THE PREPARATION OF GRIGNARD REAGENTS

BY HENRY GILMAN AND JAMES E. KIRBY

RECEIVED JANUARY 21, 1929 PUBLISHED MAY 6, 1929

Introduction

In the course of some studies on the reaction between alkyl *p*-toluenesulfonates and RMgX compounds, Gilman and Beaber[1] obtained very small quantities of an unidentified hydrocarbon melting at 119–120° in all cases where benzylmagnesium chloride was used. Later Gilman and McCracken[2] isolated the same compound, again in very small amounts, from the reaction products of nitrobenzene and benzylmagnesium chloride. More recently, in connection with an investigation of the rearrangements[3] of some Grignard reagents like benzylmagnesium chloride, the same hydrocarbon was obtained as an extremely minor product of the reaction between formaldehyde and benzylmagnesium chloride.

Inasmuch as the hydrocarbon was obtained in three widely different reactions of benzylmagnesium chloride, it appeared probable that the compound was formed independently of the reagent brought into reaction with the benzylmagnesium chloride, and must have formed during the preparation of benzylmagnesium chloride. Several check experiments soon confirmed this, for the compound was obtained, again in very small quantities, when benzylmagnesium chloride was hydrolyzed. The compound was finally shown to be di-p-tolyl. Its identity was confirmed by a series of mixed melting-point determinations between the product of the several reactions[4] and with each of these compounds and an authentic specimen of di-p-tolyl.

The most reasonable explanation, at present, for the formation of di-*p*-tolyl is the preliminary formation of free radicals in the preparation of Grignard reagents. This idea finds support in some experimental work presented recently by Gilman and Fothergill[5] on the disproportionation of free alkyl radicals probably formed incidental to the preparation of some alkylmagnesium halides. These two independent series of observations

---

[1] Gilman and Beaber, THIS JOURNAL, 47, 518 (1925).

[2] Gilman and McCracken, *ibid.*, 51, 821 (1929).

[3] See p. 1826 of an article by Gilman and Harris, *ibid.*, 49, 1825 (1927).

[4] The Experimental Part describes other reactions from which the di-*p*-tolyl was subsequently isolated in connection with studies on the course of the reaction.

[5] Gilman and Pothergill, THIS JOURNAL, 50, 3334 (1928). This article contains leading references to other related studies.

have set us in pursuit of the free radicals with the hope of capturing them before they have had an opportunity to couple or to disproportionate.[6] With such capture by so-called reliable reactions to give readily identifiable compounds, we would have unequivocable proof for the prior formation of radicals in the preparation of organomagnesium halides.[7]

The following reactions might account for the formation of di-p-tolyl and other products.

$$C_6H_5CH_2Cl + Mg \longrightarrow C_6H_5CH_2— + —MgCl \quad (I)$$

$$C_6H_5CH_2— + —MgCl \longrightarrow C_6H_5CH_2MgCl \quad (II)$$

$$C_6H_5CH_2— + C_6H_5CH_2— \longrightarrow C_6H_5CH_2CH_2C_6H_5 \quad (III)$$

$$C_6H_5CH_2— \longrightarrow p\text{-}CH_3C_6H_4— \quad (IV)$$

$$p\text{-}CH_3C_6H_4— + p\text{-}CH_3C_6H_4 \longrightarrow p\text{-}CH_3C_6H_4{\cdot}C_6H_4CH_3\text{-}p \quad (V)$$

The free radicals[8] formed in accordance with Reaction I combine to a very large extent to give benzylmagnesium chloride (Reaction II). Gilman, Zoellner and Dickey[9] have just shown that the yield of benzylmagnesium chloride is about 95%, and that this yield is independent of the rate of addition of benzyl chloride to magnesium and ether. The yield of dibenzyl formed in accordance with Reaction III is about 3 to 5%, and the yield of di-p-tolyl (see Reactions IV and V) is about 0.2 to 0.3%.

Reaction IV is illustrative of the rearrangement of the benzyl radical to a p-tolyl radical. It is highly improbable that the benzyl radical would rearrange to any appreciable extent to a *m*-tolyl radical. However, it is reasonable to expect that if a free benzyl radical is formed it should rearrange to an o-tolyl radical, and to an extent probably less than that of its rearrangement to a p-tolyl radical. Should the benzyl radical rearrange not only to the p-tolyl radical but also to the o-tolyl radical, then one might expect, in addition to di-p-tolyl, compounds like the following: *o*- and p-methyldiphenylmethane, 2,2′-dimethyldiphenyl and 2,4′-dimethyldiphenyl. The presence of an o-tolyl linkage should reveal itself in the formation of phthalic acid when the very small quantities of oils were oxidized. Evidence, in this manner, for the presence of an o-tolyl linkage was obtained by the characteristic sensitive fluorescein test with a quantity of material that was too minute for isolation. It is obvious from the

---

[6] A preliminary report of these studies was read by Gilman, Fothergill, Kirby and McGlumphy at the September, 1928, meeting of the American Chemical Society held at Swampscott, Massachusetts.

[7] A recent, very interesting, article by Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927), on the mechanism of the Wurtz–Fittig reaction may be conveniently interpreted by assuming the intermediate formation of free radicals. They give references to other related studies on the Wurtz–Fittig reaction.

[8] The excellent work of Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927), on magnesious halides has definitely added these abnormally valenced complexes to the growing series of free radicals.

[9] Gilman, Zoellner and Dickey, ibid., 51, 1576, 1583 (1929).

very large yield of Crignard reagent and the appreciable yield of dibenzyl that very little of the benzyl chloride remained to form other products.[10]

The very small percentage of di-p-tolyl made it desirable to study other possible explanations for the origin of this compound in the preparation of benzylmagnesium chloride, Quite naturally, a first consideration turns on the purity of the benzyl chloride. There is the possibility that' our benzyl chloride, even though of high purity, might contain some p-chlorotoluene. If such p-chlorotoluene were present, it might react with the magnesium[11] to form p-tolylmagnesium chloride and a small quantity of the normal[5] coupling product, di-p-tolyl. However, the possibility of the benzyl chloride being contaminated with a small amount of *p*-chlorotoluene was ruled out by two experiments. First, when a mixture of equivalent quantities of benzyl chloride and p-chlorotoluene was added to sufficient magnesium in ether to react with both halides, no p-tolylmagnesium chloride was formed[12] and, also, there was practically no di-p-tolyl. Second, the oxidation of our benzyl chloride gave benzoic acid, and none of the p-chlorobenzoic acid that might have been expected if p-chlorotoluene were present as an impurity.[13]

We would not have it understood that there is an inflexible ratio between the yields of dibenzyl and di-*p*-tolyl formed from the benzyl radical. Variations were noted in the several hydrolysis experiments. Furthermore, in two experiments that were purposely selected to give large quantities of coupling products, we found that the customary small amounts of di-p-tolyl were formed along with comparatively extremely large quantities of dibenzyl. These two experiments were the reactions with benzyl-

[10] We have little doubt that extremely large-sized preparations of benzylmagnesium chloride would reveal coupling products, in workable amounts, of compounds other than dibenzyl and di-p-tolyl. It is not a particularly inviting procedure for us to prepare very large quantities of any RMgX compound and then decompose it by hydrolysis. On p. 159 of Vol. **3** of the "Annual Survey of American Chemistry" we directed attention, in connection to the work of Bachmann and Clarke (see ref. 7 of this paper), to the special contributions to organic chemistry by manufacturers and dealers in research chemicals. For the immediate purposes of the present study, there is no imperative need for the isolation and identification of the several other possible compounds already mentioned, and which would be formed to a very small extent.

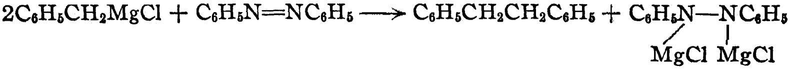
[11] Such reaction would be highly favored by the strong positive catalytic effect of benzylmagnesium chloride, a Grignard reagent that forms with great ease. See Gilman, Peterson and Schulze, Rec. *trav. chim.*, 47, 19 (1928), for a comparative study of various catalysts. Aryl chlorides form the corresponding Grignard reagents with great difficulty.

[12] This was shown by the absence of any p-toluic acid when the reaction mixture was treated with carbon dioxide prior to hydrolysis.

[13] See the Experimental Part for a discussion of the Beilstein flame test for our benzoic acid and that of several samples of "halogen-free benzoic acid" kindly supplied us by others.

magnesium chloride and cupric chloride[14] and azobenzene,[15] respectively. The following are typical reactions

$$2C_6H_5CH_2MgCl + 2CuCl_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + Cu_2Cl_2 + 2MgCl_2 \qquad \text{(VI)}$$



$$2C_6H_5CH_2MgCl + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + C_6H_5\underset{MgCl}{N}{-}\underset{MgCl}{N}C_6H_5 \qquad \text{(VII)}$$

Attention should also be directed to the possibility of the free radicals forming only with the hydrolysis of the benzylmagnesium chloride, and not being present prior to the formation of the Grignard reagent. For example, Gilman and Fothergill[15] obtained evidence for disproportionation and therefore for free radicals when they hydrolyzed some of the *alkyl*-magnesium halides studied by them. But they also showed that the same disproportionation took place to a greater extent *before* hydrolysis. By analogy, therefore, the greater part of the coupling products from benzylmagnesium chloride were formed prior to hydrolysis. Unlike the gaseous products of coupling and disproportionation that result from the preparation of alkylmagnesium halides having an R group of low molecular weight, it would be difficult to isolate the essentially non-volatile products like dibenzyl and di-p-tolyl without destroying the benzylmagnesium chloride, in whole or in part.[16]

Experimental Part

Hydrolysis of Benzylmagnesium Chloride.—A one-mole preparation of benzylmagnesium chloride was hydrolyzed by iced hydrochloric acid and the resulting mixture was steam distilled. The forerun of this steam distillate when separated, dried and distilled at atmospheric pressure gave 66.3 g. or a 72.1% yield of toluene. As soon as a sample of the original steam distillate gave crystals on cooling, the receiver was changed and the next liter of steam distillate gave 2.8 g. or a 3.1% yield of pure dibenzyl. The succeeding 550 cc. of steam distillate gave 0.25 g. (or 0.3%) of a crystalline solid melting unsharply between 85 and 90°. After 3 crystallizations of this solid from 95% alcohol, the compound melted at 119–120° and was identified as di-p-tolyl. A careful fractionation by crystallization of the dibenzyl mentioned above gave no di-p-tolyl. The 2.4 g. of dark brown non-steam distillable oil was oxidized by potassium dichromate in dilute sulfuric acid to give benzoic acid, no other carbonyl-containing compound and an oil. Oxidation of this oil by alkaline permanganate gave benzoic acid.

In a second one-mole run, the toluene fraction was distilled under reduced pressure in order to avoid the possible formation of *p*-benzyldibenzyl, inasmuch as Fuson[17] has shown that dibenzyl and benzyl chloride combine under the influence of heat to form

---

[14] Gilman and Parker, THIS JOURNAL, 46, 2823 (1924). This article contains leading references to earlier work on this coupling reaction.

[15] Gilman and Pickens, *ibid.*, 47, 2406 (1925). Gilman and Fothergill, *ibid.*, 50, 867 (1928) (see footnote 5 on p. 868 of this article by G. and F.). Also, Rheinboldt and Kirberg, *J. prakt. Chem.*, 118, 1 (1928).

[16] In this connection it is interesting to note that ethylmagnesium bromide can be refluxed in a *p*-cymene solution (b. p. 175°) without decomposition [see Gilman and Peterson, *Rec. trav. chim.*, 48, 247 (1929)]. Also, it is possible to prepare some ether-free Grignard reagents by the direct application of heat.

[17] Fuson, THIS JOURNAL, 48, 2937 (1926).

p-benzyldibenzyl. We wished to avoid the formation of this compound in order to restrict the origin of any terephthalic acid (resulting from oxidation of the small residues) to such coupling products as di-*p*-tolyl and *p*-benzyltoluene. From this run there was obtained 66.3% of toluene, 5.4% of dibenzyl and 0.2% of di-p-tolyl. Oxidation of the residues gave benzoic acid but no phthalic and no terephthalic acids. In a search for carbonyl compounds that might have resulted from such oxidation, a few drops of a light yellowish oily oxime was obtained; this showed no tendency to crystallize.

From a third one-mole run prepared by the very rapid[18] addition of benzyl chloride there was obtained 60.7% of toluene, 3.85% of dibenzyl and 0.2% of di-p-tolyl. The 1.9 g, of non-volatile oil resulting from the steam distillation was oxidized by alkaline permanganate. When the filtered oxidation mixture was acidified a slight cloudiness indicative of a trace of terephthalic acid[19] appeared. However, the quantity was altogether too small to permit of isolation. The resulting water solution was thrice extracted with ether and the ether solution, after drying, was evaporated to dryness. The solid acids were extracted with chloroform in order to isolate any phthalic acid. Only a trace remained undissolved and this appeared to be phthalic acid, inasmuch as it gave a good fluorescein test when warmed with resorcinol and sulfuric acid. Evaporation of the chloroform extracts gave 0.13 g. of benzoic acid. It should be mentioned here that oxidations in search of acids were regularly carried out with all fractions, both of steam distillates and residues, that were not definitely shown to be toluene, dibenzyl or di-*p*-tolyl.

Benzylmagnesium Chloride, p-Chlorotoluene and Carbon Dioxide.—A mixture of 0.1 mole of benzyl chloride and 0.1 mole of p-chlorotoluene was added to 0.2 atom of magnesium in ether. The resulting solution of RMgCl compound or compounds was treated with carbon dioxide in the customary manner and then hydrolyzed. The phenylacetic acid (7.0 g. or 51%) melted sharply at 76–77°, and fractional crystallization of it yielded no p-toluic acid. The yield of recovered *p*-chlorotoluene was 87.3%.

Oxidation of Benzyl Chloride.—The benzoic acid obtained by the alkaline permanganate oxidation of 0.1 mole of the benzyl chloride used in these studies gave no positive sodium fusion test for halogen. However, it did give a weak Beilstein copper wire color test. The faint green flame test appeared momentarily and without excessive heating of the wire. Because of the very critical nature of this test (a positive test would indicate the presence of p-chlorotoluene in our benzyl chloride) it was also carried out with several samples of halogen-free benzoic acid.[20] To our great surprise all four samples of such halogen-free benzoic acid (which showed no halogen after a sodium fusion test) gave a slight positive Beilstein test.

The weak Beilstein test with our several samples of benzoic acid prompted a like test with other supposedly pure carboxylic acids. The faint Beilstein test is not shown by all carboxylic acids, for among the 9 acids tested there was no positive flame test with salicylic, diphenylacetic and terephthalic acids. Should our "halogen-free benzoic acids" actually contain a trace of halogen sufficient to give this very delicate flame test

---

[18] This was carried out prior to the experiments (see ref. 9) on the effect of rapid addition of halide on the yield of RMgX compound. At that time it was believed that a rapid addition would favor the formation of coupling products and so improve the opportunity of obtaining coupling products in addition to the dibenzyl and di-p-tolyl previously isolated.

[19] At the time these studies were carried out a technique had been acquired for the isolation and identification of small quantities of the phthalic and other acids. See ref. 3 of this paper.

[20] In this connection the authors wish to express their appreciation for samples provided by Dr. H. T. Clarke and Dr. E. K. Bolton.

it still would not affect seriously our conclusions in view of the experiment (described above) on benzylmagnesium chloride, *p*-chlorotoluene and carbon dioxide. The tests with the several benzoic acids are sufficiently important to warrant further study, and we are collecting samples of benzoic acid which (as well as we can determine) are free of any hereditary and acquired taint of halogen.

Benzylmagnesium Chloride and Cupric Chloride.—From the reaction carried out in the customary manner[1]* between 0.3 mole of benzylmagnesium chloride and 0.3 mole of cupric chloride there was obtained a 70% yield of pure dibenzyl and a trace of di-*p*-tolyl. The 4.6 g. of non-steam distillable tar gave only benzoic acid on oxidation.

Benzylmagnesium Chloride and Azobenzene.—From one mole of benzylmagnesium chloride and 0.44 mole of azobenzene there was obtained 52.3% of benzidine and 37% of dibenzyl.

Benzylmagnesium Chloride and Formaldehyde.—Formaldehyde was led over the surface of 0.4 mole of benzylmagnesium chloride until a negative color test[21] was obtained showing that all of the Grignard reagent had been used up. In addition to a 26.9% yield of o-tolylcarbinol there was obtained about 0.3 g. of di-p-tolyl.

The authors gratefully acknowledge helpful suggestions from Dr. N. J. Beaber and Dr. H. T. Clarke.

Summary

Di-*p*-tolyl is formed in very small quantities incidental to the preparation of benzylmagnesium chloride. The presence of this coupling product is advanced as additional evidence for the preliminary formation of free radicals in the preparation of Grignard reagents.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE YIELDS OF SOME GRIGNARD REAGENTS. ALTERNATING PROPERTIES OF NORMAL ALKYL BROMIDES

BY HENRY GILMAN, E. A. ZOELLNER AND J. B. DICKEY

RECEIVED JANUARY 21, 1929 PUBLISHED MAY 6, 1929

Introduction

In connection with studies on the relative reactivities of alkyl and aryl halides toward magnesium in ether,[1] it was necessary to determine the yields of some Grignard reagents. These yields were determined under optimal conditions. They differ in several instances from the yields previously determined in this Laboratory.[2] In general, because of an improved mode of preparation and refinements in analytical procedure, the yields are

---

[21] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925), and Bull. *soc. chim.*, 41, 1479 (1927).

[1] A preliminary account of these studies has been reported by Gilman and Zoellner, THIS JOURNAL, 50, 2520 (1928).

[2] (a) Gilman and Meyers, *ibid.*, 45, 159 (1923); (b) Gilman and McCracken, *ibid.*, 45, 2462 (1923); (c) Gilman and McCracken, *Rec. trav. chim.*, 46, 463 (1927). Marvel, Blomquist and Vaughn, THIS JOURNAL, 50, 2810 (1928), have determined the yields of some Grignard reagents prepared in di-n-butyl ether.

somewhat higher than those reported earlier. Where the same compounds have been analyzed, the present results are to be preferred. Also, determinations have been made of the yields of a number of compounds not previously studied by us,

An examination of the yields under these standard conditions reveals an apparent alternation with the first members of the *normal* alkyl bromide series. A consideration of this phenomenon together with some general conclusions are given in the Discussion of Results.

Experimental Part

Method of Analysis.—The general analytical procedure was one of the five methods investigated by Gilman, Wilkinson, Fishel and Meyers[3] for the quantitative estimation of Grignard reagents, namely, the acid titration method. Two variations were made.

First, phenolphthalein was used throughout as the indicator. Methyl orange is an unsatisfactory indicator because of individual differences on what constitutes a true end-point, and because of general difficulties in observing color changes when arylmagnesium halides are titrated. A comparative study was made of three indicators: phenolphthalein, methyl red and methyl orange. Three pairs of aliquots from a given preparation of phenylmagnesium bromide were titrated with phenolphthalein, methyl red and methyl orange, and the average titration values with these three indicators were 94, 95.9 and 97.1%, respectively. Also, two pairs of aliquots from a preparation of *n*-butyl chloride when titrated with phenolphthalein and methyl red as indicators showed the titration value with methyl red as the indicator to be about 1.5% higher than that with phenolphthalein.

These differences, selected from several comparative titrations with the different indicators, might have been predicted, in part. Variations of about the same order were noted when magnesium sulfate (of about the quantity and concentration present in a typical Grignard analysis) was titrated with standard alkali, using the three indicators specified.

These results are of decided importance with reference to the *actual* quantity of Grignard reagent present. Gilman, Wilkinson, Fishel and

---

[3] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923). See also Gilman and Meyers, ***Rec. trav. chim.,*** 45,314 (1926), for a confirmation of our analytical procedure and a criticism of another method. The acid titration method has been extensively employed in a variety of studies in this Laboratory. (See refs. 1 and *2* in this paper and other studies from this Laboratory on organomagnesium halides.) It has also been used by others. More recent references to its application by others are to be found in studies by Marvel, Blomquist and Vaughn, THIS JOURNAL, 50, 2810 (1928), and Meisenheimer and co-workers, Ber., 61, 708, 720, 2079 (1928), who also used phenolphthalein as an indicator incidental to an acid titration that was combined with an analysis for halogen by the Volhard method. They (Meisenheimer and co-workers) recommend methyl red when no analysis is to be made for halogen.

Meyers[3] and Gilman and Meyers[2] showed that the quantity of Grignard reagent as determined by the acid titration method is generally about 4% too high, when reference is made to the more exact gas analysis method also studied by them.[2] This is so because the acid titration method, unlike the gas method,[4] is a measure of the Grignard reagent originally present, but not all of which is now available because of partial decomposition by traces of moisture, etc., to give basic compounds of the type formed from undecomposed Grignard reagent in the acid titration method of analysis. Accordingly, the use of phenolphthalein as an indicator removes almost entirely the sole serious objection to the acid titration method. This is so because with phenolphthalein the yield of a given aliquot is about 3% less than that determined when methyl orange is used as the indicator, and it was with methyl orange as an indicator that the earlier[2] quantitative studies showed the acid titration to give values about 4% higher than the gas method. Therefore, with phenolphthalein the results are only about 1% higher than those determined by the gas method.

A second variation in the acid titration procedure was in the heating with an excess of standard sulfuric acid prior to the back titration with standard alkali. In the earlier studies[2] it was recommended that the basic magnesium compounds be heated with the standard acid not over 60° in order to avoid any oxidation of hydriodic acid that might be present when alkyl or aryl iodides were used. It was shown, in the present study, that there is no difference (within experimental error) when aliquots are heated to 60° or boiled for fifteen minutes. This was demonstrated with n-butylmagnesium iodide and phenylmagnesium bromide.

Chemicals.—All of the halides, originally of the highest commercial purity, were carefully dried and distilled prior to use. The commercial magnesium turnings were crushed in a dry porcelain mortar and separated from the fine particles. The magnesium so obtained ($^1/_{12}$ to $^3/_8$-inch mesh) was essentially of uniform size. The commercial anhydrous ether was further dried by standing over sodium wire.

The following quantities of materials were used in each experiment: **0.05** mole of alkyl or aryl halide; **0.054** atom of magnesium; **30** cc. or about 6 molecular equivalents of ether and a crystal of iodine which weighed about **0.04** g.

Apparatus.—The special reaction flask used in previous[2,3] studies was simplified. The external delivery tube and stopcock, through which was forced (by gas pressure) the sample for analysis, was removed. These accessory parts for obtaining aliquots are not only unnecessary but also somewhat troublesome because of the need of freeing the open end of products formed by atmospheric decomposition of the Grignard reagent. Aliquots were quickly removed by means of clean 10-cc. pipets. With an ordinary refined technique there is very little opportunity for atmospheric decomposition.

The new simpler reaction flasks have a wider bore (15 mm. instead of 12 mm.) in the graduated necks. This did not decrease essentially the accuracy of a reading, but it did make it possible to use a more efficient stirrer.

---

[4] See Gilman and Fothergill, This Journal, 50, **3334** (1928), for additional comments (p. **3339**) on the gas method of analysis.

Procedure.—Inasmuch as this standard procedure will be referred to in several subsequent reports, it is given completely at this time.

The weighed magnesium turnings were placed in the clean reaction flask which had just previously been removed from an electric drying oven heated at about 110°.[5] The flask was then attached to an apparatus consisting of a mercury-sealed stirrer, a Hopkins condenser provided at its upper end with a drying tube filled with calcium chloride and a 100-cc. dropping funnel. After cooling the flask, 6.5 cc. of ether and the crystal of iodine were added. Then the halide, previously weighed out in a 50-cc. glass-stoppered Erlenmeyer flask, was added to the dropping funnel, and 20 drops (about 0.2 cc.) of the undiluted halide was added to the flask. This mixture was refluxed, without stirring,[6] by means of a water-bath kept at 45°.[7] The remaining 23.5 cc. of ether was used to rinse the halide from the Erlenmeyer flask, in which it was weighed, to the dropping funnel. The stirrer was then started and allowed to continue at about 750 r. p. m.

The ether–halide mixture was then added, at room temperature, over a thirty to thirty-five-minute period, by a carefully regulated rate of addition of about 15 drops per ten seconds. When all of the ether–halide had been added, the reaction continued of itself for about three to ten minutes with the alkyl halides and for about ten to forty-five minutes with the aryl halides. Stirring was continued during these additional periods as long as there was any evidence of reaction (as noted by bubbling on the surface of the reaction mixture when stirring was transitorily interrupted). When there was no further evidence of reaction, the mixture (while still being stirred) was refluxed by means of a hot-plate. The time of such refluxing was, in general, five and ten minutes for alkyl halides and fifteen and thirty minutes for aryl halides.[8]

The flask was then cooled in a bath of tap water (12–15°) and during the addition of the diluent (ether or benzene) to bring the contents up to about the 100 cc. mark, the rate of stirring was increased to about 2500 r. p. m. and kept there for two minutes to assure intimate mixing. The flask was then disconnected, stoppered and allowed to stand for five minutes[9] in the tap-water bath in order to permit settling of the magnesium particles. The volume was then read and two 10-cc. aliquots were pipetted off

---

[5] In this manner we were assured that the reaction flask was dry. The water condenser was also dry, because when not attached to the reaction flask the lower end was closed by a tight-fitting cork. The upper end was always provided with a drying tube filled with calcium chloride. Moisture has an anti-catalytic effect which must be considered in studies of relative rates of formation of Grignard reagents.

[6] See Gilman, Peterson and Schulze, Rec. *trav. chim.*, 47, 19 (1928).

[7] In this manner all reactions were permitted to start before adding the main portion of halide. This preliminary procedure also removes any incidental traces of moisture and contributes to a more uniform activation of the magnesium.

[8] By these times we mean that in one run of a given RX compound the period of refluxing was five minutes, for example, and in another run of the same halide the period of refluxing was ten minutes. In this manner it was possible to learn whether the mixture had been sufficiently refluxed so that additional refluxing would not increase the yield. In general, it was found that refluxing at the end of the reaction increased the yield 2–5%.

[9] A longer time of standing (up to one-half hour) showed no difference within the experimental error of two aliquots. The experimental error in titration of two aliquots of a given run is 0.1 to 0.2 cc. of the standard acid. If the variation were greater than 0.25 cc. of acid with the two aliquots, another aliquot was removed from the flask, which was kept in the tap-water bath for such rare variations. These variations are equivalent to 0.7–1.5% in the final yield of the Grignard reagent.

and added to 500-cc. Erlenmeyer flasks containing 150 cc. of distilled water. Sufficient standard acid (about 0.2 *N*) was added so that about 10 cc. of standard base was required in the back-titration with standard sodium hydroxide (about 0.2 N). Phenolphthalein was used as the indicator and the pipets, of course, were carefully rinsed with the acid solution and with water. Prior to the back-titration, the acid solution was heated at about 70–80° and the titration was carried out with this hot solution.

Number of Determinations and Accuracy of Method.—The yield of each alkyl halide was determined **3** times, and from each determination at least 2 aliquots were taken for analysis. The analyses checked in a surprisingly satisfactory manner when one considers the nature of the reaction. For example, in **3** separate experiments with ethylmagnesium bromide the average yields (based on at least 2 aliquots from a given experiment) were 93.4, 92.9 and 92.9%; with *n*-butylmagnesium bromide they were 94.0, 94.1 and 93.8%; and, with n-hexylmagnesium bromide 91.8, 91.6 and 92.7%.

A concordance of this high order indicates that 2 instead of **3** independent analyses of a given halide should have sufficed. However, for some reason as yet unknown, there was a greater variation with the *sec.*-butyl- and *sec.*-amylmagnesium bromides. For example, 4 runs of *sec.*-butylmagnesium bromide gave the following results: 78.4, 75.9, 79.7 and 75.5%.

Only two runs were made with each *aryl*magnesium bromide and the yields agreed within 1%.

The yields given in Table I are the averages of 2 or **3** or 4 separate runs, from each of which at least 2 aliquots were removed for analysis.

TABLE I

AVERAGE PERCENTAGE YIELDS OR RMgX COMPOUNDS

Halide used	Yield of RMgX compd., %	Halide used	Yield of RMgX compd., %
Ethyl bromide[a]	93.1	n-Heptyl bromide	88.8
n-Propyl bromide	91.7	n-Octyl bromide[c]	88.4
Isopropyl bromide	84.0	n-Butyl chloride[d]	91.2
n-Butyl bromide	94.0	n-Butyl iodide[e]	85.6
Isobutyl bromide	87.2	Benzyl chloride	93.1
Sec.-butyl bromide	77.7	Bromobenzene[f]	94.7
Tert.-butyl bromide	25.1	*o*-Bromotoluene[g]	92.7
n-Amyl bromide	88.6	*m*-Bromotoluene	88.0
Iso-amyl bromide	88.0	*p*-Bromotoluene	86.9
Sec.-amyl bromide[b]	66.8	α-Bromonaphthalene[h]	94.8
Tert.-amyl bromide	23.7	β-Bromonaphthalene	83.8
n-Hexyl bromide	92.0		

[a] Because of the volatility of ethyl bromide several runs were made with an extra condenser. However, this added precautionary measure did not give any higher results than those obtained with the one condenser used with all other halides.

[b] The 66.8% yield is the average of 4 experiments which in turn averaged 69.5, 69.6, 65.8 and 62.3%.

[c] The original pure commercial sample of n-octyl bromide boiled between **197–200.5°** (uncorr.). This was distilled before use and the fraction boiling between **198–**

200.5° gave yields of 87.4 and 88.5%. On redistillation of the halide a fraction boiling at 200–201° was collected and this gave a yield of 89.2%.

[d] The average yields of 3 runs were 89.8, 92.1 and 91.6%. In the 89.8% yield run there was evidence of a reaction one hour after all of the halide had been added, and in this run the mixture was refluxed for twenty minutes. In the 92.1% yield run there was evidence of reaction after one hour and ten minutes. This mixture was then stirred an additional one and one-half hours and then refluxed for thirty minutes. The 91.6% yield run was like the 92.1% run with the exception of a two-hour (instead of a thirty-minute) period of refluxing.

[e] The 85.6% yield of n-butylmagnesium iodide is from freshly distilled iodide. In two other runs where the iodide was distilled one month prior to use the yield was 3–4% lower. Some bromides, like n- and *iso*butyl and phenyl, showed essentially no difference in yield whether the commercially pure compounds were distilled or not distilled.

[f] There was evidence of reaction ten minutes after all of the bromobenzene was added. The mixture was then refluxed for ten minutes. With the exception of *n*-butyl chloride, bromobenzene appeared to react for a longer time than any alkyl bromide after all of the halide had been added.

[g] The three bromotoluenes appeared to react thirty-five to fifty minutes after all of the halide was added. They were then refluxed for fifteen and thirty minutes, respectively, in alternate runs in order to assure completeness of reaction (see ref. 8 of this paper).

[h] The bromonaphthalenes appeared to react twenty to thirty minutes after all of the halide was added. They were then refluxed for fifteen and thirty minutes, respectively, in alternate runs. Benzene was used as a diluent in the experiments with the bromonaphthalenes in order to bring the solutions to the 100-cc. mark. Methyl orange is an unsatisfactory indicator under these conditions. The naphthylmagnesium bromides were, of course, prepared in the 30 cc. of ether, but like RMgBr compounds from p-bromoanisole and p-bromophenetole, they or their etherates are sparingly soluble in ether and more soluble in an ether–benzene mixture.

Discussion of Results

Alternation of Normal Alkyl Bromides.—A glance at the yields of *normal* alkylmagnesium bromides from propyl to heptyl reveals an apparent alternation. The even-numbered halides give yields higher than the *preceding* halides that have an odd number of carbon atoms. This alternation may be accidental. However, we are inclined to doubt that this is the case because the differences are well beyond any experimental error in the method of analysis.

If this alternation is not fortuitous, then methylmagnesium bromide might be expected, under the conditions of our experiments, to give a yield less than that of ethylmagnesium bromide. The difficulty of handling methyl bromide, although not overly serious, might be sufficient to throw some doubt on values obtained with it. Furthermore, results with it might be open to various interpretations because of the known irregularities of first members of homologous series.

Octyl bromide, on the basis of alternation, should give a higher yield of the Grignard reagent than heptyl bromide. The only indication of a higher yield is found in the single experiment described in Footnote (c) of Table I. Possibly, if the phenomenon of alternation is sound, it may become very weak or disappear entirely at the octyl bromide level.

It is interesting to recall that in the earlier studies by Gilman and McCracken[2b] attention was directed to an apparent alternation with normal iodides. Here, however, the odd-numbered iodide gave a higher yield than the preceding iodide having an even number of carbon atoms. This alternation broke down completely, as was mentioned at that time, in the case of propyl iodide, which gave a distinctly lower yield of Grignard reagent than did ethyl iodide.

For those who would seek an explanation of the observed alternations it is well to remember that the reaction of an RX compound with magnesium in ether is not simple. All that we have measured here is the quantity of Grignard reagent that formed. Several minor side reactions have been considered recently by Gilman and Fothergill.[4]

Decrease in Yield with Ascent of Series.—There is no doubt concerning the general and gradual drop in yield in a given series with the ascent of that series to halides of higher molecular weight. However, this drop is so gradual that it is necessary to revise drastically ideas that are still current concerning the decided drop in yield (to 50% or so) with hexyl or octyl

Effect of Branching.—With a given series, the order of decreasing yield is normal, secondary and tertiary. Special conditions are necessary for the preparation of tertiary Grignard reagents in distinctly satisfactory yields. These have been described by Gilman and Zoellner.[11]

Reactivity of Halogen.—With a given R group (the n-butyl, for example) the lowest yields are with the iodide and the highest with the bromide. The alkyl chlorides react quite slowly, and if sufficient time is taken it is possible that the chlorides will be found to give higher yields than (or yields at least as high as) the corresponding bromide.

The chlorine in benzyl chloride and the bromine in allyl bromide are decidedly more active than the chlorine in n-butyl chloride and yet all three have given yields in excess of 90%. Different types of halides must be handled differently in obtaining optimum yields of the corresponding Grignard reagents. This is strikingly illustrated with benzyl chloride and allyl bromide, each of which has a highly reactive halogen. For example, benzyl chloride can be added at once to magnesium in ether and yet give

[10] The sustained high yields are strikingly illustrated by the as yet unpublished work of Houben and Bodler, a brief account of which is given in Houben-Weyl, "Die Methoden der Organischen Chemie," 4, 725, second edition, published in Leipzig in 1924. It is interesting to note (private communication from Professor Houben) that phenolphthalein was used as an indicator in their titrations. See also ref. 4 in the article by Gilman and Meyers, *Rec. trav. chim.*, 45, 314 (1926).

[11] Gilman and Zoellner, THIS JOURNAL, 50, 425 (1928); Rec. *trav. chim.*, 47 (1928).

an excellent yield of benzylmagnesium chloride (see following paper); whereas if allyl bromide is added at once to magnesium in ether, very little allylmagnesium bromide results, and most of the allyl bromide couples to form diallyl. However, by the special conditions described recently by Gilman and McGlumphy[12] it is possible to obtain allylmagnesium bromide in greater than 90% yields.

The Naphthylmagnesium Bromides.—The yield of α-naphthylmagnesium bromide reported earlier[ab] is incorrect. This was very probably due to the sparing solubility of this Grignard reagent in ether (see footnote *h* to Table I). The comparatively high yield of β-naphthylmagnesium bromide is both interesting and valuable in view of the discouragingly low yields of this RMgBr compound reported by others.[13]

The authors gratefully acknowledge assistance from R. W. Borgeson and L. L. Heck.

Summary

The yields of a number of typical Grignard reagents have been determined. Where comparisons can be made with earlier determinations these revised yields are higher. Attention is directed to a number of generalizations, particularly the apparent alternation in yields with the n-alkyl bromides.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE EFFECT OF RAPID ADDITION OF HALIDE ON THE YIELDS OF SOME GRIGNARD REAGENTS

BY HENRY GILMAN, F. A. ZOELLNER AND J. B. DICKEY

RECEIVED JANUARY 21, 1929 PUBLISHED MAY 6, 1929

Introduction

In studies on the relative reactivities of alkyl and aryl halides toward magnesium in ether,[1] all of the halide is added at once to the magnesium in ether and the reaction is interrupted at regular intervals to determine the rate of reaction. This makes it necessary to have comparative values showing the yields of Grignard reagent when all of the halide is added at once. Yields under such conditions have been determined and are here reported. The results of such studies have an importance over and above

---

[12] Gilman and McGlumphy, *Bull. soc. chim.*, 43, 1322 (1928).

[13] Loevenich and Loesser, *Ber.*, 60, 320 (1927), reported a 28.5% yield of β,β'-dinaphthyl and no β-naphthoic acid when their reaction product of β-bromonaphthalene and magnesium was treated with carbon dioxide. Probably the highest yield of a compound from β-naphthylmagnesium bromide is a 50% yield of β-naphthaldehyde reported by Chichibabin, *Ber.*, 44, 443 (1911).

[1] A preliminary account of these studies has been reported by Gilman and Zoellner, THIS JOURNAL, 50, 2520 (1928).

their value for rate studies. These considerations are treated in the Discussion of Results.

Experimental Part

The general design of the apparatus,[2] the quantities of reagents, the starting of the reaction, the rate of stirring, the conclusion of the reaction and the method of titration were identical with the procedure described in the preceding paper by Gilman, Zoellner and Dickey.[3] The reaction was started with 20 drops (about 0.2 cc.) of halide in 6.5 cc. of ether and a crystal of iodine weighing about 0.04 g.

Then 23.5-cc. of ether was added to the remainder of the halide contained in the dropping funnel. The stirrer was started and kept at a rate of about 750 r. p. m., and the halide and ether were added as rapidly as possible. The time of addition was about ten seconds.[4] All reactions were allowed to continue at room temperature and from time to time stirring was interrupted to ascertain evidence of any reaction. When the reaction was apparently concluded, the mixture was treated in the manner described in the preceding paper.

Approximate times were noted when there was no evidence of reaction subsequent to the rapid addition of all of the halide. For the alkyl halides[5] and benzyl chloride this time was nine to twelve minutes; for bromobenzene it was about twelve to fifteen minutes; and for the other aryl halides the time was about one hour.

The average yields with rapid addition given in Table I are of at least two independent runs. The widest variation between any pair of runs was 2.5%. Each run in turn is an average based on at least two aliquots which agreed between 0.7% and 1.5%.[3] For purposes of comparison, Table I also includes the average percentage yield under optimal conditions and the difference between these two yields, namely, the average percentage drop in yield with rapid addition of halide.

Discussion of Results

A glance at Table I shows that there is a drop in yield with each of the compounds studied when the halide is added rapidly. This might have been predicted in view of the results obtained by Gilman and Meyers[6] in their study of the optimal conditions for the preparation of ethylmagnesium iodide. They showed that the yield of ethylmagnesium iodide was 93.3% when the ethyl iodide was added over a forty-five minute period and 85.2% when the ethyl iodide was added as rapidly as possible, which was about thirty seconds under the conditions of those experiments. With this result as a basis, all later investigations in this Laboratory[7] on optimal conditions for other Grignard reagents incorporated, among other factors, a slow rate of addition.

---

[2] The bore of the graduated neck of the reaction flask was 20 mm. instead of 15 mm. This greater width was necessary in order to reduce the accumulation of reaction mixture in the neck of the flask as a consequence of the vigorous reaction attendant on the rapid addition of halide.

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929).

[4] In the earlier study by Gilman and Meyers, *ibid.*, 45, 159 (1923), the time for the rapid addition of ethyl iodide was about thirty seconds.

[5] See preceding paper for the slow reaction with n-butyl chloride.

[6] Gilman and Meyers, THIS JOURNAL, 45, 159 (1923).

[7] Literature references to these articles are given in footnotes 2b, 2c, 11 and 12 of the preceding paper (ref. 3); see also footnote *d* to Table I of this paper.

TABLE I

AVERAGE: PERCENTAGE YIELDS OF RMgX COMPOUNDS APTER RAPID ADDITION OF HALIDE, AND DECREASE IN YIELDS FROM NORMAL ADDITION

Halide Used	Yield, opt. cond. %	Yield, hal. added rapidly, %	Diff. or drop in yield, %	Halide Used	Yield. opt. cond. %	Yield, hal. added rapidly, %	Diff. or drop in yield, %
Ethyl bromide	**93.1**	86.6	6.5	n-Heptyl bromide	88.8	72.9	15.9
n-Propyl bromide	**91.7**	82.5	9.2	n-Octyl bromide	88.4	73.3	15.1
Isopropyl bromide	**84.0**	70.5	13.5	n-Butyl chloride	91.2	90.6	0.6
n-Butyl bromide	**94.0**	79.2	14.8	*n*-Butyl iodide	85.6	67.8	17.8
Isobutyl bromide[a]	**87.2**	76.7	10.5	Benzyl chloride	93.2	92.9	0.3
Sec.-butyl bromide[b]	**77.7**	61.6	16.1	Bromobenzene	94.7	89.8	4.9
Tert.-butyl bromide[c]	**25.1**	17.8	7.3	b-Bromotoluene	92.7	88.3	4.4
n-Amyl bromide	**88.6**	73.2	15.4	m-Bromotoluene	88.0	81.3	6.7
Iso-amyl bromide	**88.0**	70.2	17.8	*p*-Bromotoluene	86.9	83.3	3.6
Sec.-amyl bromide[b]	**66.8**	49.2	17.6	a-Bromonaphthalene	94.8	91.7	3.1
Tert.-amyl bromide	**23.7**	19.1	4.6	β-Bromonaphthalene[d]	83.8	81.3	2.5
n-Hexyl bromide	**92.0**	77.2	14.8				

[a] The 10.5% drop in yield is the average of three independent runs. The third, which agreed closely with the other two, was made because it is difficult to understand why the drop in yield with isobutyl bromide should be less than the drop with *n*-butyl bromide and *iso*-amyl bromide.

[b] Three independent runs were made with *sec.*-butyl and *sec.*-amyl bromides in order to note any possible irregularity with these halides.[3] The several runs gave good checks.

[c] Three independent runs were made with *tert.*-butylmagnesium bromide and all checked within 0.6%.

[d] A greater drop in yield was expected with β-naphthylmagnesium bromide because Loevenich and Loesser, Ber., 60, **320** (1927), reported a 28.5% yield of β,β'-dinaphthyl and no β-naphthoic acid when their reaction product of β-bromonaphthalene and magnesium was treated with carbon dioxide (see ref. **13** of ref. **3.**)

However, the extent of the drop in yield could not have been predicted with any exactitude in several of the compounds studied. First, benzylmagnesium chloride shows practically no drop in yield with rapid addition. This is astonishing in view of the statements in the literature that unless special precautions are taken in the preparation of this Grignard reagent the yield of coupling product (in this case, dibenzyl) can reach 30%. Second, the drop in yield with *tert.*-butyl- and *tert.*-amylmagnesium chlorides is less than one might have expected in view of the studies by Gilman and Zoellner[8] on the optimal conditions for the preparation of these *tertiary* Grignard reagents. They found it necessary to add the tertiary halides extremely slowly (about two to three hours) in order to get a good yield of the RMgCl compound. However, consideration should be given to the fact that there is already a very marked drop in yield from the very special conditions of Gilman and Zoellner[8] for the two tertiary chlorides, and the

---

[8] Gilman and Zoellner, THIS JOURNAL, 50, **425** (1928); *Rec.* trav. chim., 47, **1058** **(1928).**

more general conditions of Gilman, Zoellner and Dickey[3] for all types of Grignard reagents. In the former case the yield was 58%[9] in a two-hour period of addition and in the latter case about 25% in a 30 to 35 minute period of addition.

In general the alkyl halides show a greater drop in yield on rapid addition than do the aryl halides. With the alkyl halides the iodide shows a greater drop than the bromide and the bromide, in turn, shows a greater drop than the chloride. With an R group of a given weight, the branched-chain isomers show a greater drop than the normal or straight-chain compound.[10]

The greater drop of the alkyl halides over the aryl halides makes an explanation based on the greater activity of the halogen in alkyl halides very attractive. However, over and against any rigid interpretation on this basis is the almost insignificant drop with benzyl chloride, a halide that contains halogen that is comparatively highly reactive.[11] Quite probably a correlation will be found on the basis of some studies now in progress on the preliminary formation of free radicals in the preparation of organometallic compounds.[12]

The results obtained in this study have a practical value for synthetic purposes. For example, benzylmagnesium chloride can be prepared in excellent yield by the rapid addition of halide, and a reasonably rapid rate of addition can be used for the preparation of the arylmagnesium halides investigated without serious impairment in yield. The results also emphasize the necessity of special methods for the preparation in optimum yields of different types of RMgX compounds.

It is interesting to note, particularly from a preparative viewpoint, that in a rapid addition of halide there is little to be gained in having the reaction start with *a* small part of the halide prior to the rapid addition of practically all of the halide. With all the experiments reported in Table I the reaction was started with 20 drops of the halide and a crystal of iodine. In other experiments with several typical halides (n-butyl bromide, benzyl chloride and bromobenzene) it was observed that the yield was only about 1% lower than those reported when *all* of the halide was added at once (with or without the addition of a crystal of iodine).

---

[9] The yield of *tert.*-butylmagnesium chloride is appreciably higher (at least 69.5%) in larger sized runs (about 2.5 moles).*

[10] We have no explanation at present for the lesser drop of isobutylmagnesium chloride (10%) when compared with that of iso-amylmagnesium chloride (17.8%); see footnote a of Table I,

[11] We should again like to direct attention to the fact that the rapid addition of allyl bromide to magnesium in ether gives little allylmagnesium bromide. However, Gilman and McGlumphy, Bull. *soc. chim.*, 43,1322 (1928), have shown that this Grignard reagent can be obtained in yields greater than 90% by the slow addition of allyl bromide to an excess of finely-divided magnesium.

[12] Gilman and Fothergill, THIS JOURNAL, 50,3334 (1928); also Giman and Kirby, *ibid.*, 51, 1571 (1929).

Summary

A study has been made of the drop in yield of Grignard reagents when the halide is added very rapidly to magnesium in ether and some generalizations have been drawn from these results.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

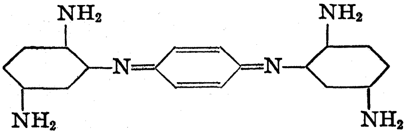
THE CONSTITUTION OF BANDROWSKI'S BASE

BY JOHN J. RITTER AND GUNTHER H. SCHMITZ

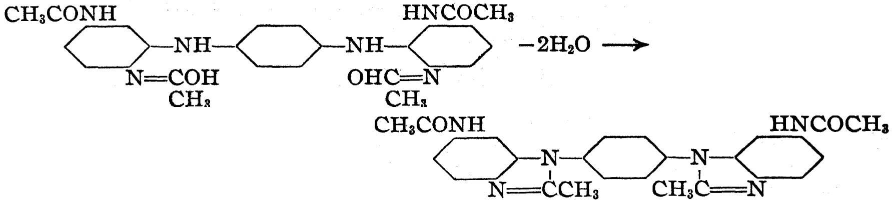
RECEIVED JANUARY 22, 1929 PUBLISHED MAY 6, 1929

Introduction

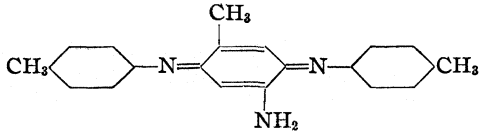
Bandrowski[1] obtained, on ferricyanide oxidation of p-phenylenediamine in aqueous ammoniacal solution, a product to which he assigned the structure shown. This constitution is based on elementary analysis, molecular



weight determination, production of p-phenylenediamine on zinc-dust distillation, the formation of a tetra-acetyl derivative, and ring-closure with the formation of a dipyrazole on reduction of the tetra-acetyl derivative, as follows



In view of the fact that p-toluidine has been shown by Barsilowski[2] and Green[3] to yield on oxidation a base of the formula (A), it appears quite

A


possible that p-phenylenediamine might behave similarly, to yield **the** following isomer (B) of the Bandrowski base. Its properties, as observed

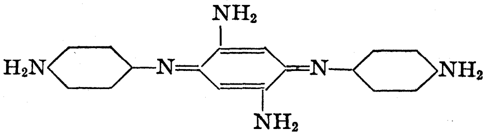
---

[1] Bandrowski, *Monatsh.*, 10, 123 (1889); *Ber.*, 27, 480 (1894).

[2] Barsilowski, *ibid.*, 6, 1209 (1873); *ibid.*, 8, 695 (1875).

[3] Green, *ibid.*, 26, 2772 (1893).

B



by Bandrowski and by others,[4] up to the present fail to establish either structure as the correct one. Comparison of the two will show their ability to respond to all of the known reactions of the substance. Our attention was also arrested by the fact that the oxidation of p-phenylenediamine does not proceed further under the conditions of the experiment. The second structure, in which para-diamine groupings capable of assuming the quinoid structure are absent, is in closer harmony with this behavior than the first, in which the two non-quinoid nuclei might be expected to oxidize readily. The present work was undertaken to throw some light on this point.

We have now succeeded in obtaining evidence which confirms the structure already assigned to the substance. This was accomplished by the method of Willstatter and Dorogi,[5] in which quinone-imides were oxidized with yields of 85–95% to benzoquinone with lead peroxide and sulfuric acid. The benzoquinone obtained was determined by the method of J. Rzymkowski[6] by titration against sodium thiosulfate solution, using Wurster's indicator (pamidodimethylaniline). It is apparent, by comparison of the two alternative formulas, that one mole of the substance of the first formula can yield but one-third of a mole of quinone on oxidation, while one mole of a substance of the second formula should yield two-thirds of a mole of quinone. The results of several experiments confirm the former structure, which is therefore the correct one.

Experimental Part

Preparation of Bandrowski's Base.—This substance was prepared both by the use of potassium ferricyanide and of hydrogen peroxide as oxidizing agents; the latter was found to yield a pure product directly. In a typical experiment, 10 g. of *p*-phenylenediamine (recrystallized once from benzene) was dissolved in 750 cc. of water to which 3 cc. of concentrated ammonia solution had been added, and the solution was treated with 125 cc. (2.5 moles) of 3% hydrogen peroxide solution. After standing for twenty-four hours at room temperature, 2 g. of pure oxidation product was filtered off. Further portions were filtered off after similar time intervals. After seventy-two hours three portions thus separated totaled 3.6 g. The first portion, consisting of well-defined bronze leaflets, was of high purity. The material separating subsequently consisted of finer particles which seemed to be somewhat contaminated with foreign matter. In the experiments to be described, only that portion first separating was used, after drying to constant weight at 100°; m. p. 238° (corr.).

---

[4] A. Heidushka and E. Goldstein, *Arch. Pharm.*, **254**, 584–625 (1916); R. Willstatter and Mayer, *Ber.*, **37**, 1505 (1904); E. Erdmann, *ibid.*, **37**, 2908 (1904).

[5] Willstatter and Dorogi, *ibid.*, **42**, 2166 (1909).

[6] Rzymkowski, *Z. Elektrochem.*, **31**, 371–382 (1925).

Oxidation of the Base to **Benzoquinone.**—Five g. of lead peroxide and 5 g. of concd. sulfuric acid were ground together in a mortar until a uniform thin paste was obtained. This was added slowly, with cooling, to 25 cc. of 25% sulfuric acid, contained in a 100 cc. Erlenmeyer flask. To this mixture a weighed amount (about 0 3 g.) of the base was added, the mixture shaken until the base had completely dissolved, stoppered loosely and allowed to stand for twenty-four hours. At the end of this time, the resulting solution was of a clear yellow color. The benzoquinone was extracted from the aqueous acid solution by repeated shaking with small amounts of ether (10 cc. at a time), in the reaction vessel. The ethereal washings were separated by decantation and combined. This operation was repeated until a fresh portion of the ether extracted nothing further from the reaction mixture, six to eight such extractions being sufficient. The final extract is recognized by the fact that it is colorless and leaves no residue on evaporation. That the combined ethereal extracts contained pure benzoquinone was determined in one experiment by evaporation of a portion and determination of the melting point of the solid thus obtained, without recrystallization. It was found to melt at 115°, while pure benzoquinone has the recorded melting point of 115.7".

Analysis of the Ethereal Extracts.—An approximately equal volume of water and 3 cc. of glacial acetic acid were added to the ethereal solution of benzoquinone and the mixture was titrated against standard sodium thiosulfate solution. The ether–water mixture was well shaken after each addition of thiosulfate. The color of the quinone may be used as indicator, or *p*-amidodimethylaniline may be used externally. The latter method was found to give a sharper end-point and more concordant results and was used throughout. Benzoquinone and sodium thiosulfate react in dilute acetic acid solution as follows[e]

$$2C_6H_4O_2 + 4H^+ + 2S_2O_3^= = C_6H_2(OH)_2(S_2O_3H)_2 + C_6H_4(OH)_2$$

Standardization of the Sodium Thiosulfate Solution.—The thiosulfate solution used was standardized against twice resublimed benzoquinone, using *p*-amidodimethylaniline as indicator: (1) 0.2032 g. of quinone in 50 cc. of water and 3 cc. of acetic acid used 20.27 cc.; (2) 0.3342 g. of quinone in 50 cc. of water and 3 cc. of acetic acid used 33.40 cc.; therefore 1 cc. of thiosulfate = 0.0100 g. of quinone.

TABLE I

ANALYTICAL RESULTS

Sample, g.	Thiosulfate, cc.	Quinone. g.	Calcd. for $^1/_3$ mole	Calcd. for $^2/_3$ mole	% of $^1/_3$ mole	% of $^2/_3$ mole
0.3116	9.57	0.0957	0.1058	0.2116	90.4	45.2
.3045	9.00	.0900	.1034	.2068	87.0	43.5
.2901	9.00	.0900	.0985	.1970	91.4	45.7

Summary

1. The yield of benzoquinone obtained by oxidation of Bandrowski's base by lead peroxide and sulfuric acid has been determined.
2. The results of such determinations confirm the constitution previously assigned to the compound.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

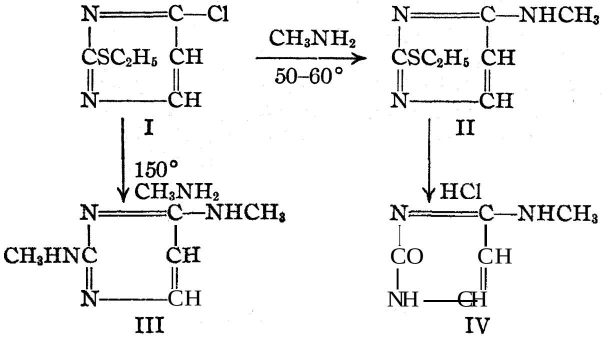
THE SYNTHESIS OF A NEW METHYLCYTOSINE

BY FRANCIS H. CASE WITH ARTHUR J. HILL

RECEIVED FEBRUARY 5, 1929 PUBLISHED MAY 6, 1929

Preliminary to a study of the action of diazomethane on certain nucleic acids and on the pyrimidine constituents[1] of the same it became necessary, for identification purposes, to synthesize a new methylcytosine, 2-oxy-6-methylaminopyrimidine, IV.

The method[2] which has been successfully employed utilizes as the starting material 2-ethylmercapto-6-chloropyrimidine, I. When this substance is treated with an absolute alcohol solution of methylamine in an autoclave the reaction proceeds in one of two ways, depending largely on the temperature factor.



At 50–60° the product is the hydrochloride of 2-ethylmercapto-6-methylaminopyrimidine, II, while at 150° the ethylmercapto group is displaced and the hydrochloride of 2,6-di-(methylamino)-pyrimidine, III, is formed. The free bases are easily obtained from the corresponding hydrochlorides by treatment with alkali.

The methylated cytosine, IV, is readily prepared, in the form of its hydrochloride, by digesting 2-ethylmercapto-6-methylaminopyrimidine, II, with concd. hydrochloric acid. The free base is obtained from the hydrochloride by careful treatment of the latter with potassium hydroxide in absolute alcohol. It gives a characteristic picrate and a positive color test[3] (purple) with bromine, indicative of the absence of a substituent in position 3.

Experimental Part

Hydrochloride of 2,6-Di-(methylamino)-pyrimidine.—Nine grams of 2-ethylmercapto-6-chloropyrimidine[2] was heated in an autoclave at 150° for four hours with

---

[1] Preliminary paper, *Proc. Nat. Acad. Sci.*, 8, 44 (1922).

[2] Wheeler and Johnson, Am. Chem. J., 29, 492 (1903).

[3] Wheeler and Johnson, J. *Biol.* Chem., 3, 183 (1907).

4 molecular proportions of methylamine in absolute alcohol solution. At the end of this period the autoclave was opened and a strong odor of ethyl mercaptan was observed. After removal of tarry material by filtration, the filtrate was evaporated to dryness and the residue crystallized several times from absolute alcohol. The hydrochloride melts at 262° and is soluble in water and alcohol, but insoluble in ether and acetone.

Anal. Calcd. for $C_6H_{11}N_4Cl$: N, 32.10; Cl, 20.33. Found: N, 31.88, 32.11; Cl, 20.50, 20.34.

2,6-Di-(methylamino)-pyrimidine, 111.—Four grams of the hydrochloride of 2,6-di-(methylamino)-pyrimidine was dissolved in absolute alcohol and treated with an absolute alcohol solution of potassium hydroxide to faint alkalinity. The potassium chloride was filtered off and the filtrate evaporated to dryness. The residual base, after three crystallizations from a ligroin-absolute alcohol mixture, melted constantly at 132°. It is soluble in water and absolute alcohol, and insoluble in ligroin, acetone and ether.

Anal. Calcd. for $C_6H_{10}N_4$: N, 40.57. Found: N, 40.13, 40.21.

The Hydrochloride of 2-Ethylmercapto-6-methylaminopyrimidine.—Nine grams of 2-ethylmercapto-6-chloro-pyrimidine was heated in an autoclave for four hours at 50–60° with an absolute alcohol solution of 3.5 molecular proportions of methylamine. There was no perceptible odor of ethyl mercaptan upon opening the autoclave and the solution was clear, with entire absence of gummy material. It was evaporated to dryness and the residue triturated with ether. The precipitate of methylamine hydrochloride was filtered off and washed with ether. Dry hydrogen chloride was then passed into the ethereal filtrate until precipitation was complete; the precipitate was filtered and weighed (9 g.). After two crystallizations from an acetone–absolute alcohol mixture, the hydrochloride melted at 216". It is soluble in water and absolute alcohol, but insoluble in ether and acetone.

Anal. Calcd. for $C_7H_{12}N_3S{\cdot}Cl$: N, 20.44; S, 15.57. Found: N, 20.58, 20.52; S, 15.62.

When this reaction was carried out at 105–110°, a mixture of 2,6-di-(methylamino)-pyrimidine and 2-ethylmercapto-6-methylaminopyrimidine was formed, with the latter considerably in predominance.

2-Ethylmercapto-6-methylaminopyrimidine, 11.—When the above-described hydrochloride was dissolved in water and treated with concd. ammonium hydroxide, the free base was precipitated as an oil, which solidified on standing. It was filtered and then dissolved in a mixture of ligroin and absolute alcohol. From this solvent it separated as an oil which solidified when triturated with ligroin. The pure base thus obtained melts at 58°; it is insoluble in water, sparingly soluble in ligroin and very soluble in alcohol.

Anal. Calcd. for $C_7H_{11}N_3S$: N, 24.85. Found: N, 24.95, 24.77.

Hydrochloride of **2-Oxy-6-methylaminopyrimidine.**—2-Ethylmercapto-6-methylaminopyrimidine was digested for eight hours with concentrated hydrochloric acid; the resulting solution was then evaporated to dryness and the residue crystallized from aqueous alcohol. It crystallizes in small prisms which decompose at 320°. It is soluble in water and insoluble in alcohol, acetone and ether.

Anal. Calcd. for $C_5H_8N_3OCl$: N, 26.01; Cl, 21.95. Found: N, 25.90, 26.07; Cl, 22.28, 22.21.

2-0x9-6-methylaminopyrimidine, IV.—One and six-tenths g. of crude 2-oxy-6-methylaminopyrimidine hydrochloride, suspended in absolute alcohol, was treated with absolute alcoholic potash until the solution was faintly alkaline. The potassium chloride was filtered off and the filtrate evaporated to dryness. The base was purified by crystallization from aqueous acetone, out of which it separated in cubes which melted at 270°. It is soluble in water and alcohol and insoluble in acetone and ether. Unlike cytosine, this base is not hydrated. It gives the Wheeler–Johnson color test.[3]

Anal. Calcd. for $C_5H_7N_3O$: N, 33.60. Found N, 33.38, 33.30.

The picrate of 2-oxy-6-methylaminopyrimidine crystallizes from water in slender prisms and melts at 220–225°.

Summary

1. The interaction of methylamine and 2-ethylmercapto-6-chloropyrimidine produces either 2-ethylmercapto-6-methylaminopyrimidine or 2,6-di-(methylamino)-pyrimidine, depending on the temperature employed.

2. A new methylcytosine, 2-oxy-6-methylaminopyrimidine, is formed by acid hydrolysis of 2-ethylmercapto-6-methylaminopyrimidine.

NEW HAVEN, CONNECTICUT

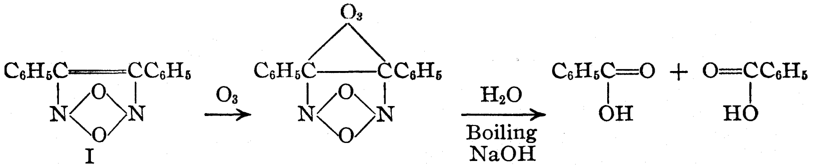
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE STRUCTURE OF FURAZAN OXIDES. II

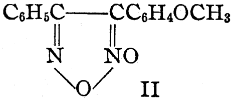
BY CORLISS R. KINNEY

RECEIVED FEBRUARY 13, 1929 PUBLISHED MAY 6, 1929

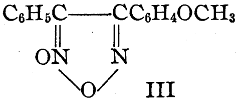
Furazan oxides (or furoxans) are attacked by ozone and the ozonized substances are decomposed with water and alkalies yielding acids. This behavior of these substances has been interpreted[1] on the basis of an ethylenic structure as follows



Meisenheimer, Lange and Lamparter,[2] however, have succeeded in isolating two substances which they believe to be isomeric furazan oxides. The isolation of two isomeric oxides does not permit an ethylenic formula, I, but necessitates an unsymmetrical structure, which in the case of Meisenheimer's oxides would have Formulas II and III.



II



III

The two isomeric oxides II and III were obtained by oxidizing the two *amphi*-dioximes of *p*-methoxybenzil. They appeared to be non-separable and isomorphous since recrystallization of a mixture from alcohol did not

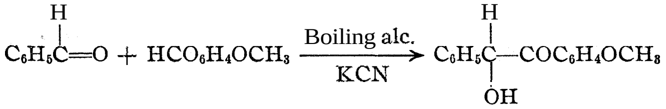
---

[1] Kinney and Harwood, THIS JOURNAL, 49, 514 (1927).

[2] Meisenheimer, Lange and Lamparter, Ann., 444, 94 (1925).

seem to change the melting point; the melting points of various mixtures was not lowered, but fell between the two extremes. In order to elucidate the mechanism of the reaction of furazan oxides with ozone, a study of Meisenheimer's two oxides has been made in this Laboratory and new and more convenient syntheses of these substances and of the oximes from which they are made developed.

Benzaldehyde and anisaldehyde have been condensed together to form *p*-methoxy-benzoin,[2a] but we are aware of no case in which an attempt has been made to condense the two aldehydes in satisfactory yields. The condensation takes place readily with the anisaldehyde adding to the benzaldehyde. This manner of reaction

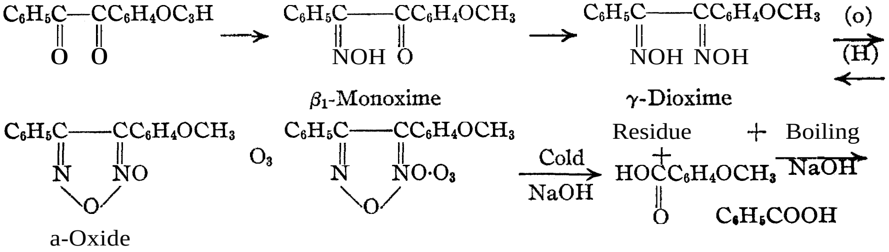


$$C_6H_5\overset{H}{\overset{|}{C}}=O + HCO_6H_4OCH_3 \xrightarrow[KCN]{\text{Boiling alc.}} C_6H_5\underset{OH}{\overset{H}{C}}—COC_6H_4OCH_8$$

is undoubtedly due to the difference in reactivity of the two carbonyl groups. Difficulty was experienced in oxidizing the benzoin derivative to p-methoxybenzil using the old nitric acid process for benzil, but the method outlined in "Organic Syntheses"[3] is to be highly recommended for *p*-methoxybenzil.

The earlier synthesis of the two oxides of phenyl-*p*-methoxyphenylfurazan involved the preparation of the two *amphi*-dioximes of *p*-methoxybenzil, which in turn were made from the two β-monoximes. When p-methoxybenzil was heated with one equivalent of hydroxylamine, the &-monoxime[4] was the exclusive product, due again to the difference in reactivity of the carbonyl groups. This prevented the direct synthesis of the α-dioxime and the β- or lower melting oxide, III; in order to synthesize this isomer we used two other methods.

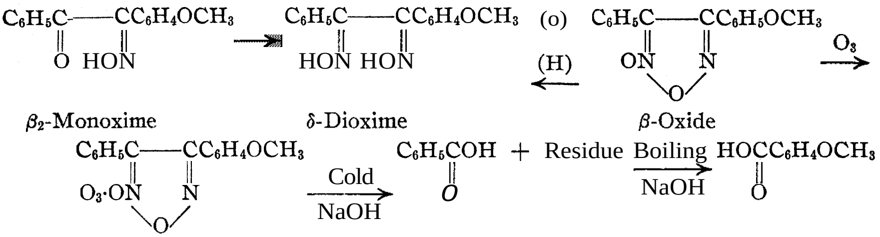
Both carbonyl groups of p-methoxybenzil were oximated at once and the resulting product, which was largely the β-dioxime, was oxidized to a mixture of the α- and β-oxides. By means of persistent fractional



[2a] Ekecrantz and Ahlquist, *Arkiv. Kem. Min.* Geol., 3, (No. 13) 1–26 (1908). See also Staudinger, Ber., 46, 3535 (1913).

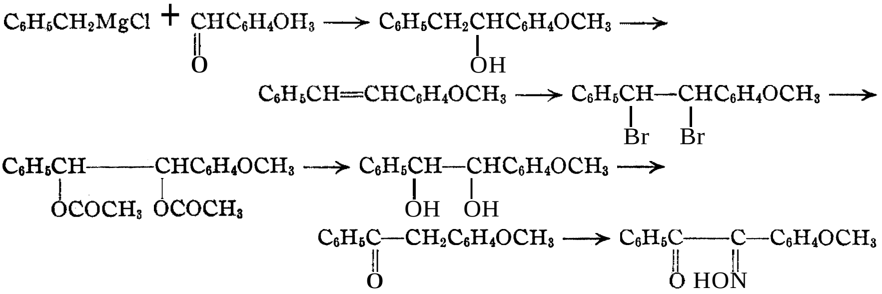
[3] "Organic Syntheses," John Wiley and Sons, Inc., New York, *6,* 6 (1926).

[4] We will use Meisenheimer's system of nomenclature.



crystallization from acetone (instead of alcohol) the two oxides were separated. About one-tenth of the product was the β-oxide.

The second method involved the synthesis of the β_2-monoxime from phenylanisyl ketone, in the following way. Owing to repeated small yields this method has little to recommend it over the above or over Meisenheimer's synthesis which involved p-methoxyphenylnitromethane as **a** starting material.



$$\mathrm{C_6H_5CH_2MgCl} + \underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{HC_6H_4OH_3} \longrightarrow \mathrm{C_6H_5CH_2}\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{C}}\mathrm{HC_6H_4OCH_3} \longrightarrow$$

$$\mathrm{C_6H_5CH{=}CHC_6H_4OCH_3} \longrightarrow \mathrm{C_6H_5}\underset{\substack{| \\ \mathrm{Br}}}{\mathrm{CH}}-\underset{\substack{| \\ \mathrm{Br}}}{\mathrm{CH}}\mathrm{C_6H_4OCH_3} \longrightarrow$$

$$\mathrm{C_6H_5}\underset{\substack{| \\ \mathrm{OCOCH_3}}}{\mathrm{CH}}-\underset{\substack{| \\ \mathrm{OCOCH_3}}}{\mathrm{CH}}\mathrm{C_6H_4OCH_3} \longrightarrow \mathrm{C_6H_5}\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{CH}}-\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{CH}}\mathrm{C_6H_4OCH_3} \longrightarrow$$

$$\mathrm{C_6H_5}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{CH_2C_6H_4OCH_3} \longrightarrow \mathrm{C_6H_5}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\underset{\substack{\| \\ \mathrm{HON}}}{\mathrm{C}}-\mathrm{C_6H_4OCH_3}$$

In general we have found the work of Meisenheimer, Lange and Lamparter on the oximes and oxides of the p-methoxy series to be quite correct except for the purity of the two oxides. By repeated recrystallizations from acetone (instead of alcohol, in which these substances are fairly insoluble cold) the a-oxide was found to melt at 108–109" and in like manner the melting point of the β-isomer was raised to 104–105° with softening at 102". The @-oxide probably was not perfectly pure even then but was sufficiently so for most purposes. The melting point of mixtures of the two purified oxides were always lower, the eutectic point being the 95–97° mixture of Meisenheimer and designated by him as the β-isomer. The two substances behave similarly chemically and are undoubtedly the isomeric furazan oxides, II and III.

The appearance of two isomeric furazan oxides disproved the ethylenic structure, I, and demands an unsymmetrical formula such as II and III. On this basis the attack of these substances by ozone cannot be explained by means of an ethylenic linkage. The imino linkage did not react with ozone in the aromatic furazans (or oxazoles). Diphenylfurazan when treated with ozone reacted slowly and did not produce acids as did the furazan oxides. The only remaining point of attack was the side of the molecule holding the extranuclear oxygen atom, that is, the NO linkage or an endoxy linkage if that be preferred. Since carbonyl groups add on ozone, it seems possible that the NO Linkage would react likewise, followed by a stepwise decomposition of the molecule.

The two isomeric oxides of phenyl-*p*-methoxyphenylfurazan reacted with ozone in the same way as the diphenyl derivative.[1] Upon decomposition with cold sodium hydroxide the a-isomer yielded anisic acid while the *β*- produced benzoic acid. The residue from the a-, when boiled with sodium hydroxide, yielded largely benzoic acid and the residue from the *β*- largely anisic acid (see diagram, pp. 1593–1594). The structural difference between the two oxides is thus clearly demonstrated.

The process of oxidation has been shown to start on the side of oxidized nitrogen and to instigate a stepwise decomposition of the molecule. The aromatic group nearer the point of attack would be the first to appear as aromatic acid and the one farther removed to appear after boiling with sodium hydroxide. All of this may be used for determining which structure to give to the individual oxides and to the dioximes from which they are obtained and into which they may be transformed.

Meisenheimer based the structures of the oximes given in the diagram largely upon his work with triphenylisoxazole and ozone;[5] they are the reverse as determined by the Beckmann rearrangement. The fnrazan oxides obtained from the *α*- and *β*-dioximes by oxidation were given structures by him corresponding to the dioxime from which they were obtained. By means of our reaction with ozone the structures assigned to the oxides by Meisenheimer must be correct, since the process of ozonization and decomposition with alkali requires that the extranuclear oxygen atom be attached nearer the p-methoxyphenyl in the a- or higher melting isomer and nearest the phenyl group in the *β*-, as shown in the diagram. Thus we have proof from a still different source as to the correctness of the configuration of the dioximes as set forth by Meisenheimer.

Experimental Part

***p*-Methoxybenzoin.**[6]—Since benzaldehyde condenses in the presence of potassium cyanide much more rapidly than anisaldehyde, we allowed benzaldehyde, in our earlier experiments, to drop slowly into a boiling alcoholic solution of anisaldehyde and potassium cyanide. This procedure was found to be unnecessary and as good yields were obtained by mixing the aldehydes at the outset. The following was our best practice.

Fifty grams of potassium cyanide was dissolved in 350 cc. of water in a 3-liter flask. To this was added 272 g. (2 moles) of anisaldehyde,[7] 212 g. (2 moles) of benzal-

---

[5] Meisenheimer, *Ber.*, 54, 3206 (1921); see also Kohler and Richtmyer, THIS JOURNAL, 50,3105 (1928).

[6] Obtained in another way by Meisenheimer with Jochelson, *Ann.*, 355, 249–311 (1907).

[7] No particular advantage was noticed with redistilled aldehydes and in most of our work Eastman's "Practical" grade was used.

dehyde[7] and 700 cc. of 95% alcohol. The mixture formed a solution at the boiling temperature and was refluxed for one and one-half hours. Steam was then passed through the solution until all of the alcohol and nearly all of the unchanged aldehydes were removed. The condensed water was decanted from the product and the latter set away to crystallize. The product was then pressed as free as possible from oily material on a suction funnel and washed with cold alcohol. In this way about 350 g. of crude product was obtained. The crude mixture was dissolved in hot alcohol and allowed to crystallize slowly. The p-methoxybenzoin crystallized out first in large clumps of long needles, while the benzoin crystallized in small compact balls of needles. With some experience a good yield of nearly pure p-methoxybenzoin can be filtered out before the appearance of the benzoin. The yield of pure p-methoxybenzoin amounted to 100–110 g. For conversion into p-methoxybenzil only two or three recrystallizations were necessary, or until the melting point reached 102 or 103°.

***p*-Methoxybenzil.**—The usual method for making benzil from benzoin by nitric acid oxidation was not applicable to the oxidation of p-methoxybenzoin. The oxidation proceeded too far and considerable oily material made a separation of the benzil derivative impractical. However, the method described in "Organic Syntheses"[3] gave an 85 to 90% yield. The procedure followed in isolating the derivative was slightly different from that given there. After the oxidation had proceeded for two hours and the pyridine-copper sulfate solution was dark green in color, the mixture was transferred while still hot to a separatory funnel and the pyridine–copper sulfate solution drawn off. Ether and 10% hydrochloric acid were then added and the mixture shaken until the odor of pyridine had disappeared. After separation of the acid layer the ether solution was partially evaporated and alcohol and water added. The substance crystallizes readily when fairly pure in spite of its low melting point. It is best recrystallized from about 80% alcohol; m. p. 62–63°; bright yellow in color.

Anal.[8] Subs., 0.2013: H_2O, 0.0886; CO_2, 0.5783. Calcd. for $C_{15}H_{14}O_3$: C, 75.0; H, 5.0. Found: C, 75.0; H, 5.04.

The γ-Dioxime of *p*-Methoxybenzil and the Preparation of the a-Oxide of Phenyl-*p*-methoxyphenylfurazan.[9]—Meisenheimer, Lange and Lamparter[2] synthesized the β-monoxime of *p*-methoxybenzil by means of a rather long and laborious process. We found that p-methoxybenzil was readily changed to the above oxime in the following way.

Forty grams of p-methoxybenzil and slightly less than one equivalent of hydroxylamine hydrochloride were dissolved in a minimum of alcohol and refluxed for one and a half hours. The solution was then poured into water and the oxime extracted with benzene. The benzene solution was extracted with 10% sodium hydroxide and the oxime precipitated with carbon dioxide. After one crystallization from benzene the melting point was 120–124° but after two recrystallizations from carbon disulfide it was raised to 129–130°. The yield was 25 g.

Three or four grams of unchanged ketone was recovered, but no β_2-monoxime. The remainder of the product did not crystallize.

The preparation and properties of the γ-dioxime and the a-oxide prepared from it are correct as given by Meisenheimer except for the melting point of the latter substance which is discussed in detail under the separation of the oxides on page 1597.

The Preparation of the Mixed Oxides of Phenyl-*p*-methoxyphenylfurazan.—The oxidation of either the a- or β-dioxime of p-methoxybenzil yields a mixture of the two oxides of phenyl-*p*-methoxyphenylfurazan.[2] However, several attempts to prepare the a-dioxime using the method for making the a-dioxime of benzil resulted in poor

---

[8] By Marcel Mayhue.

[9] By G. E. Hinckley.

yields, but the α-dioxime obtained had the melting point given by Meisenheimer and not that of the product obtained by Ponzio[10] in an entirely different manner.

Also, attempts were made to oximate the ketone using pyridine solutions. The color of the ketone was rapidly discharged, but the separation of the reaction products was not very successful. This method of oximation appeared worthy of further investigation.

Our best method for getting a dioxime for oxidation to the oxides was as follows. Twenty-four grams (0.1 mole) of *p*-methoxybenzil was dissolved in 50 cc. of alcohol, 7 g. (0.1 mole) of hydroxylamine hydrochloride dissolved in 10 cc. of water added and the whole refluxed for thirty minutes. Then 10.5 g. (0.15 mole) of hydroxylamine hydrochloride in 10 cc. of water, 15 cc. of 6 N sodium hydroxide and 35 cc. of alcohol were added and the whole boiled for forty-five minutes. Finally, 30 cc. of 6 N sodium hydroxide was added and the solution refluxed for one hour and forty-five minutes. At the end of this time the solution was diluted with a liter of water and an insoluble precipitate, probably of the furazan, filtered out. Dilute acid was added to precipitate the oximes, which were separated by decanting the water from the sticky product. The oximes were dissolved in 300 cc. of 6 N sodium hydroxide and diluted to 4 liters. Sodium hypochlorite made from 10% sodium hydroxide and chlorine was added to the above solution (cooled by addition of ice) until no more precipitation occurred. The precipitated oxides were recrystallized from acetone and petroleum ether (or alcohol). The first crop weighed 12.7 g. (m. p. 99–102°); the second, 1.5 g. (m. p. 93–95"); the third, 0.6 g. (somewhat oily).

The preparation of the dioximes can undoubtedly be improved considerably. Too early addition of sodium hydroxide cut the above yield in half. Also, the oxidation of the dioxime should not be carried out before precipitating out the oxime from the solution containing hydroxylamine. Considerable material was lost earlier in this way, as a rather strange decomposition took place. The precipitate when allowed to warm up turned green, evolved gas and finally turned into a yellow-orange liquid product. Anisic acid was formed simultaneously.

The Separation of the Phenyl-p-methoxyphenylfurazan Oxides.—Eighty-three grams of the mixed oxides obtained much as described above was fractionally crystallized from acetone and a mixture of acetone and petroleum ether. The higher melting oxide crystallized first in considerable quantities and relatively pure (m. p. 102–105°). Repeated fractions were necessary to isolate the 95–97° mixture of Meisenheimer and to isolate a higher melting product which when mixed with the a-oxide was lowered. The mixed oxides were finally separated into fractions of 58 g. of the a-oxide and 8.6 g. of lower melting β-oxide. The a-oxide after repeated recrystallizations finally melted at 108–109°. The 8.6 g. of impure p-oxide upon further fractionation yielded 4 g. of oxide melting at 104–105° with softening at 102". This was probably not perfectly pure even then since it softened below the melting point and since the products of oxidation with ozone were not as clean as with the a-oxide.

The relatively smaller yield of the (3-oxide from the β-dioxime is difficult to explain since the mechanism of the process by which the oximes are transformed into the furazan oxides is obscure. However, it seems likely that the two hydrogen atoms of the oximino groups (or, if the oxidation is carried out in an alkaline solution, the two ionic charges) are removed, leaving an unstable arrangement which at once changes into the furazan oxide. In the case of the β-dioxime the influence of the *p*-methoxyphenyl group apparently shows up in the amounts of the two isomers actually formed. The yield of the β-oxide from the α-dioxime may be greater, but we have not tried this because of insufficient quantities of the α-dioxime.

---

[10] Ponzio and Bernardi, *Gazz. chim. ital.*, 53, 813 (1923).

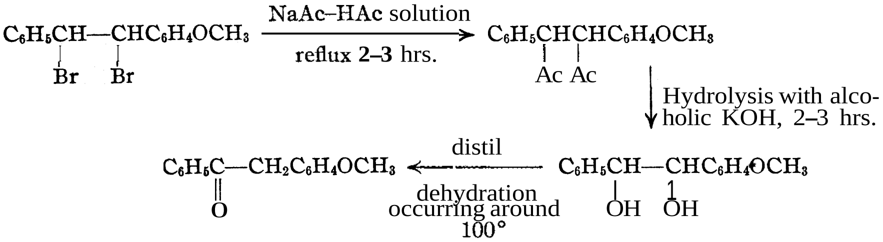
The Second Method for Preparing the β-Oxide and the Ozonization of Diphenyl Furazan[11]

p-Methoxyphenylbenzylcarbinol and p-Methoxystilbene.—p-Methoxyphenylbenzylcarbinol[12] was prepared using the Grignard reaction in the usual way. This compound has since been described in the literature and consequently will not be described here; however, we have analyses and molecular weight determination which are in good agreement. It is best recrystallized from ether and petroleum ether.

For our purpose of preparing p-methoxystilbene we did not attempt to isolate the carbinol in our later experiments, but simply distilled the crude reaction product under a water-pump vacuum. A yield of 90% of p-methoxystilbene is obtained from anisaldehyde in this way.

p-Methoxystilbene Dibromide.—Our best yield of dibromide was only 78% and often yields were much poorer. Better yields were obtained by cooling and stirring the reaction mixture (a chloroform solution was used) and by slow addition of bromine. The insoluble dibromide was purified by washing with ether.

p-Methoxydisoxybenzoin.—The p-methoxystilbene dibromide was changed into phenylanisyl ketone, $C_6H_5COCH_2C_6H_4OCH_3$, by the following reactions



$$\underset{\mathrm{Br}}{\mathrm{C_6H_5CH}}\text{—}\underset{\mathrm{Br}}{\mathrm{CHC_6H_4OCH_3}} \xrightarrow[\text{reflux 2–3 hrs.}]{\text{NaAc–HAc solution}} \underset{\mathrm{Ac}}{\mathrm{C_6H_5CH}}\underset{\mathrm{Ac}}{\mathrm{CHC_6H_4OCH_3}}$$

$$\Big\downarrow \text{Hydrolysis with alcoholic KOH, 2–3 hrs.}$$

$$\underset{\mathrm{O}}{\overset{\|}{\mathrm{C_6H_5C}}}\text{—}\mathrm{CH_2C_6H_4OCH_3} \xleftarrow[\text{dehydration occurring around 100°}]{\text{distil}} \underset{\mathrm{OH}}{\mathrm{C_6H_5CH}}\text{—}\underset{\mathrm{OH}}{\mathrm{CHC_6H_4OCH_3}}$$

No attempts were made to isolate intermediate substances. The diacetate was obtained from the acetic acid solution by diluting with water and decanting the solution from the sticky acetate. The mixed hydrobenzoin was obtained from the alcoholic solution in much the same way except that it was collected and introduced into the distilling flask using ether as a solvent. The yields were 30–40%.

β_2-Monoxime of p-Methoxybenzil.—Nine grams of phenylanisyl ketone was dissolved in 50 cc. of dry alcohol and 10 cc. of sodium ethylate solution, prepared from 1 g. of sodium, added. To this solution cooled to 0° was slowly added 7 g. of amyl nitrite. The orange-colored solution was set away in a cool place for twenty-four hours. The oxime was then extracted with 10% sodium hydroxide solution and precipitated by passing carbon dioxide into the solution until saturated.

The oxime was purified by solution in 10% sodium hydroxide and reprecipitation with carbon dioxide, followed by recrystallization from hot alcohol. The yield was 3.6 g. or 36% and the melting point 169–170°. Considerable amounts of p-methoxystilbene appeared at this point, probably coming from a different dehydration process than the one outlined for the hydrobenzoins; that is, our phenylanisyl ketone was not perfectly pure.

The Change of the **β_2-Monoxime** into the 8-Oxide.—The δ-dioxime of **p-methoxybenzil** is not very stable and the purification is complicated because of its tendency to form compounds with molecules of the solvent of crystallization. Consequently in

---

[11] By H. J. Harwood.

[12] The general method for preparing p-methoxydesoxybenzoin or phenylanisyl ketone was that as outlined in C. *A*., 20, 2324 (1926); abstract of a paper by Orekhoff and Tiffeneau, ***Bull.*** *soc.* chim., 37, 1410–1420 (1925).

our work we usually oxidized the freshly prepared crude δ-dioxime, prepared according to Meisenheimer, Lange and Lamparter.[2] It seemed advantageous to precipitate the dioxime either with very dilute sulfuric acid or by adding sodium bicarbonate and then redissolve the oxime in fresh 10% sodium hydroxide and proceed with the oxidation according to Meisenheimer. The product melted at 95–97° when recrystallized from alcohol. Several recrystallizations from alcohol, in which it is fairly insoluble when cold, did not change the melting point. However, carefully repeated fractionations from other solvents does change the melting point as described under the fractionation of the mixed oxides.

The Ozonization of **Diphenylfurazan.**—One gram of diphenylfurazan was ozonized in nearly the same manner as diphenylfurazan oxide in the earlier experiments. Since the ozonizer was giving about 4% ozone instead of 3% as formerly, the furazan was ozonized for six hours instead of seven. When treated with sodium hydroxide in the same way as the corresponding oxide, not a trace of benzoic acid was obtained and 0.72 g. of the unchanged furazan was recovered.

The Ozonization of the Oxides of **Phenyl-*p*-Methoxyphenylfurazan.**—The ozonization of the oxides of *p*-methoxydiphenylfurazan was carried out as before in pure dry carbon tetrachloride as a solvent. The presence of a drop of water did not materially alter the process of oxidation, although it slowed down the rate. One-gram samples were used and a stream of ozonized oxygen containing 3–4% of ozone was passed through for nine to twelve hours. Usually, after running the ozone for about six hours the solutions stood about twenty hours (overnight) and then ozone was passed through for three to six hours more. This procedure, of course, materially lengthened the time the oxides were in contact with the ozone.

A non-explosive, sticky yellow product separated in each case after six hours' running, which could not be purified even when larger runs were made. Starting with diphenylfurazan oxide only benzoic acid could be isolated from the insoluble substance. In contact with alkalies it turned red and slowly dissolved. From the alkaline solution only benzoic acid could be obtained.

In ozonizing the *p*-methoxydiphenylfurazan oxides no attempt was made to work with the insoluble product, but 10% sodium hydroxide was added at once and the whole shaken until the ozonides had dissolved, forming a red solution. The carbon tetrachloride solution was extracted a second time with a little sodium hydroxide and finally the mixed sodium hydroxide solutions were extracted with ether and acidified. In order to ascertain the total amount of acid product, especially where benzoic acid was concerned, the acidified solution was extracted with ether two or three times. After evaporating the ether the crude acid yield was determined. The kind of acids present was ascertained by recrystallization from hot water.

The carbon tetrachloride solution above was next evaporated to a yellow liquid, which was dissolved in alcohol containing some 10% sodium hydroxide. The solution became red and after boiling for thirty minutes was diluted with water and the water extracted with ether. The water solution was acidified, extracted and the amount and kind of acid present determined as before. The residue after the extraction with boiling alcoholic sodium hydroxide was small, usually about 0.1 g. and was not the unchanged oxide.

One gram of the α-oxide after ozonization and extraction with cold 10% sodium hydroxide yielded from 0.5 to 0.6 g. of crude anisic acid. After one crystallization from hot water the acid melted at 163–164°. A second crystallization raised the melting point to 173–176°, the product still retaining some color. In a mixed melting point with an authentic specimen of anisic acid the melting point rose to 179–180°. The weight of crude acid after boiling with sodium hydroxide varied from 0.35 to 0.43 g.

Upon crystallization from hot water the melting point was 115–118° and a mixture with benzoic acid melted at 118–119°.

One gram of the β-oxide yielded after the first treatment 0.35 g. of acid. The acid was dissolved in boiling water and after cooling slightly deposited a few crystals of anisic acid. The next crop was 0.1 g. of impure benzoic acid melting at 90–95°, while remaining in solution was fairly pure benzoic acid as determined by extraction and crystallization from a smaller volume of water. Thus the crude acid was found to be largely benzoic acid.

After boiling the residue with alcoholic potassium hydroxide for one and a half hours, 0.8 g. of crude acid was obtained. The crude acid was heated with water and 0.2 g. failed to dissolve. From the water 0.5 g. of impure anisic acid was obtained, m. p. 140–50°. Recrystallization and mixed melting point determinations showed it to be anisic acid. The remaining 0.2 g. in solution was impure benzoic acid.

The Action of the Grignard Reagent on the Oxides of **Phenyl-*p*-methoxyphenylfurazan.**—Phenylmagnesium bromide in excess reacted readily with the furazan oxides, the experiments of Wieland and Semper[13] notwithstanding. Considerable heat was evolved when the reaction with diphenylfurazan oxide was allowed to proceed without cooling. There was no apparent reaction for some time, but in the end it became violent, distilling out the ether and leaving a very tarry residue. The oxides were entirely altered by allowing them to stand for two or three hours with phenylmagnesium bromide cooled with ice water. Phenol and diphenyl appeared in relatively large amounts. The quantities of these products did not vary greatly whether the reaction mixture was kept cold, refluxed after addition of the oxide or the oxide added to a boiling benzene solution of phenylmagnesium bromide. The amount of diphenyl was usually about one-half mole per mole of oxide and the amount of phenol isolated as tribromophenol between one-half and one mole. By boiling the Grignard product with alcoholic potassium hydroxide, ammonia was evolved and a semi-solid acid fraction obtained which smelled of benzoic acid. The residue from this treatment when boiled with hydroxylamine and alcoholic potassium hydroxide yielded small amounts of oximes of the type of benzophenone-oxime.

Many attempts were made to get a reaction with the oxides of phenyl-*p*-methoxyphenylfurazan and phenylmagnesium bromide in a way that would show up their differences in structure. They both yield phenol and diphenyl, but mixtures of benzophenone-oxime and probably *p*-methoxybenzophenone-oxime were obtained. This was to be expected to a certain extent from the work of Angeli[14] and Bigiavi.[15]

Summary

A study of the isomeric oxides of phenyl-*p*-methoxyphenylfurazan has been made. It has been shown that the two substances are not isomorphous. The structural difference between them has been clearly demonstrated by the reaction with ozone followed by a stepwise decomposition. The determination of the individual structures of the oxides by means of the ozone reaction gives further proof that the configurations of the oximes, to which the oxides are closely related, are correct as set forth by Meisenheimer.

SALT LAKE CITY, UTAH

---

[13] Wieland and Semper, *Ann.*, **358**, 36 (1908); see also Wieland, *ibid.*, 424, 107 (1921).

[14] Angeli, *Gazz. chim. ital*, *46*, *300* (1916); *Atti Accad. Lincei*, (V) 25 [2] **7** (1916).

[15] Bigiavi, *Gazz. chim. ital.*, [2] **51**, 324 (1921).

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY,
PULP AND PAPER RESEARCH INSTITUTE, MCGILL UNIVERSITY]

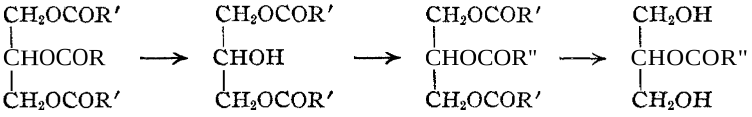
MECHANISM OF ORGANIC REACTIONS. I. THE WANDERING OF ACYL GROUPS IN GLYCEROL ESTERS

BY HAROLD HIBBERT AND NEAL M. CARTER[1]

RECEIVED FEBRUARY 20, 1929 PUBLISHED MAY 6, 1929

Introduction

Previous methods for the allocation of one or more free hydroxyl groups in derivatives of polyhydroxy compounds have often consisted in a primary esterification with an acid anhydride or halide, followed by selective hydrolysis, oxidation or degradation and, finally, identification of the resulting product as a substance of established constitution. An example of such a procedure is indicated in the following scheme



$$\begin{array}{ccccccc} CH_2OCOR' & & CH_2OCOR' & & CH_2OCOR' & & CH_2OH \\ | & & | & & | & & | \\ CHOCOR & \longrightarrow & CHOH & \longrightarrow & CHOCOR'' & \longrightarrow & CHOCOR'' \\ | & & | & & | & & | \\ CH_2OCOR' & & CH_2OCOR' & & CH_2OCOR' & & CH_2OH \end{array}$$

I II III IV

Selective hydrolysis of a glycerol ester of Type I leaves a free hydroxyl group in the β-position of II, which is then "ear-marked" by the introduction of a suitable acid radical —COR″, not readily hydrolyzable. The resulting new glycerol triacyl ester, III, is then further hydrolyzed to the glycerol monoacyl ester, IV, the constitution of which has been previously determined.

Similar schemes have been followed in the determination of the structure of fats[2,3] and of the ring forms of certain sugars and their derivatives.*

Conversely, the synthesis of mixed glycerol esters (including fats) has been accomplished by means of a primary esterification of glycerol dichlorohydrins, followed by replacement of the chlorine atoms by acyl groups either directly or through the medium of the free dihydroxy compound, as indicated below[3,5]

---

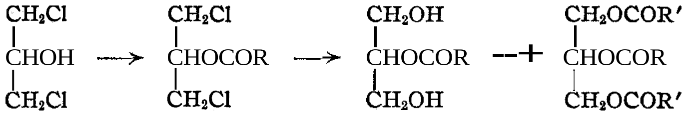
[1] Research Fellow, McGill University, Montreal. This work was carried out under the auspices of the cooperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the support accorded them.

[2] Griin and Corelli, *Z. angew. Chem.*, 25, 665, 947 (1912); Marcusson, *ibid.*, 26, 173 (1913).

[3] Griin and Wittka, *Ber.*, 54, 273 (1921).

[4] For a recent example, see Hickinbottom, *J. Chem. Soc.*, 1928, 3140.

[5] Griin and Skopnik, *Ber.*, 42, 3750 (1909); Griin, *ibid.*, 43, 1288 (1910); Whitby, *J. Chem. Soc.*, 128,1458 (1926); Thompson, *Proc.* Roy. *Soc. Canada,* [iii] 20, 445 (1926); Brash, *J. Soc. Chem. Ind.*, 46, 481T (1927).



$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CHOCOR \\ | \\ CH_2Cl \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2OCOR' \\ | \\ CHOCOR \\ | \\ CH_2OCOR' \end{array}$$

A similar, but more complex process has been utilized by Bergmann, Brand and Dreyer,[6] starting from n-dihydroxypropylamine.

The validity of the conclusions drawn from such decompositions and syntheses has, in view of an accumulating number of experimental anomalies encountered, been called into question, more especially in recent years. As long ago as 1871, Hübner and Müller[7] described the formation of allyl alcohol from α,α'-dichlorohydrin by the action of sodium in dry ether, pointing to the rearrangement at some stage of the atoms attached to an α-carbon atom. Among the more recent references to supposed migrations of substituents in glycerol derivatives may be cited the observation by Fischer[8] that glycerol α-iodohydrin-α',β-distearate, on the substitution of hydroxyl for iodine, gave glycerol α,α'-distearate. Gilchrist and Purves[9] found that the methylation of glycerol α,α'-dichlorohydrin and subsequent replacement of the chlorine atoms by hydroxyl yielded glycerol α-monomethyl ether instead of the expected β-isomer.[10] Grün and Limpacher,[11] in preparing synthetic cephalin were unable to detect any difference in the physical or chemical properties of the product prepared from either α,α'- or α,β-distearin.

The migration of a benzoyl group from the p- to the *m*-position during the hydrolysis of the acetyl groups in 3,5-diacetyl-4-benzoylgallic acid is another similar case.[12]

Attention has frequently been focused on this apparent group migration in the case of acyl derivatives of glycerol,[13] and a method for the avoidance of such in the preparation of glycerol β-esters is to be found in the proposal of Helferich and Sieber[14] to use glycerol α,α'-ditrityl ether as an intermedi-

---

[6] Bergmann, Brand and Dreyer, *Ber.*, **54, 936 (1921).**

[7] Hübner and Müller, **Ann., 159, 173 (1871).**

[8] Fischer, *Ber.*, 53, **1621 (1920).** It is of interest that the latter compound possesses a melting-point (78.5–79°) very similar to that of the glycerol *α-mono*stearate (76–77°) described by the same investigator, *ibid.*, **53, 1589 (1920).**

[9] Gilchrist and Purves, **J.** *Chem. Soc.*, **127, 2735 (1925).**

[10] These reactions are under investigation and are to be reported in the near future.

[11] **Grün** and Limpacher, *Ber.*, 60, **152 (1927).**

[12] Fischer, Bergmann and Lipschitz, *Ber.*, **51, 45 (1918).**

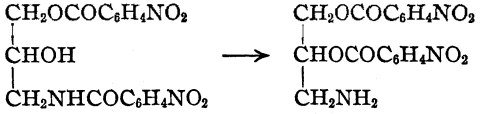
[13] (a) Grün, Wittka and Scholze, *ibid.*, **54, 273, 290 (1921);** (b) Fairbourne and Foster, **J.** *Chem. Soc.*, **128, 3148 (1926);** (c) Hill, Whelen and Hibbert, THIS JOURNAL, **50,2235 (1928);** (d) Hibbert and Carter, *ibid.*, **50,3120,3376 (1928).** After the present paper had been prepared for publication, a recent and excellent review of the conflicting evidence encountered in the structure of disubstituted glycerols, together with valuable experimental results, has appeared, Fairbourne and Cowdrey, **J.** *Chem. Soc.*, **1929,** 129.

[14] Helferich and Sieber, *Z. physiol. Chem.*, **170,** 31 **(1927).**

ate derivative, it being pointed out that trityl chloride (triphenylchloromethane) shows a preferential reactivity toward primary as compared with secondary alcoholic groups.

This tendency of groups to wander is not confined to the glycerol type. Thus the bromine atom in ethyl a-bromo-acetoacetic ester migrates to the y-carbon atom either on standing alone or in presence of a trace of hydrogen bromide;[15] 1,2-dibromo-3-butene on standing yields an equilibrium mixture with its isomer, 1,4-dibromo-2-butene;[16] the acetyl groups in octa-acetylmaltose are to be considered mobile,[17] and Karrer and Hurwitz[18] cite many acylated acetone sugars to which no definite constitution can be assigned, due to rearrangement of the acyl groups on scission of the cyclic ketal ring. The wandering of the half-acetal ring in the sugars and glucosides from one carbon atom to another is of common occurrence and may even be caused by the preference of acetone for adjacent hydroxyl groups in the formation of diacetone glucose and mannose.[19]

The migration of groups to, or from, atoms other than carbon, is of interest, although possibly of less immediate importance in the present connection. Thus the wandering of a *p*-nitrobenzoyl radical from a nitrogen to an oxygen atom[6]



$$\begin{array}{lcl} \mathrm{CH_2OCOC_6H_4NO_2} & & \mathrm{CH_2OCOC_6H_4NO_2} \\ | & & | \\ \mathrm{CHOH} & \longrightarrow & \mathrm{CHOCOC_6H_4NO_2} \\ | & & | \\ \mathrm{CH_2NHCOC_6H_4NO_2} & & \mathrm{CH_2NH_2} \end{array}$$

and the migration of an acyl group brought about by the introduction of a second acyl group[20] are instances of many other examples of this type to be found in the literature.

Migration of Acyl Groups During Cyclic Acetal Hydrolysis

These foregoing examples show that the proof of constitution by "earmarking" hydroxyl groups in tri- and poly-hydroxy compounds rests on a precarious basis. The investigations on cyclic acetal formation carried out in these Laboratories over a period of several years[13c,d,21] have had for one of their principal objects the accumulation of the necessary experimental data which might throw some light on (A) the true value to be placed on the two

[15] Hantzsch, *Ber.*, 27, 355 (1894).

[16] Thorpe, *J. Chem. Soc.*, 1928, 729.

[17] Freudenberg, Dürr and von Hochstetter, *Ber.*, 61, 1741 (1928).

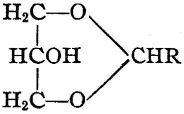
[18] Karrer and Hurwitz, *Helv. Chim. Acta*, 4, 728 (1921). A recent interesting synopsis of the migration of atoms and radicals is to be found in a series of papers by Gillet, *Bull. soc. chim. belg.*, 1921–1922.

[19] W. N. Haworth, "Constitution of the Sugars," Edward Arnold and Co., London, 1929, p. 52; Ohle and Erlbach, *Ber.*, 61, 1870, 1875 (1928).

[20] Raiford and Couture, THIS JOURNAL, 46, 2305 (1924).

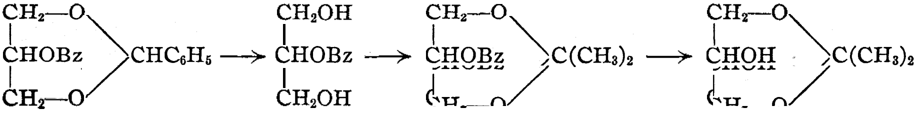
[21] Hibbert and co-workers, *ibid.*, 45, 734, 2433, 3108, 3117, 3124 (1923); 46, 1283 (1924); 50, 1411, 2235, 2242 (1928).

main processes of methylation, namely, (a) use of silver oxide and methyl iodide[z2] and (b) dimethyl sulfate and caustic soda[z3] as applied to carbohydrates and polysaccharides for the purpose of determining their structure, and (B) the tendency and ease of "ring-shift" in the furanose and pyranose rings present in such derivatives. In the course of these investigations, the constitution of the structurally isomeric cyclic acetals of glycerol was determined by the use as reference compounds of a- and β-monomethyl ethers of glycerol.[13c,d]



A consideration of the structure of a typical six-membered glycerol cyclic acetal would indicate that this should prove a valuable product for the preparation of glycerol β-derivatives as, for example, the pure glycerol β-esters, through the medium of which might be prepared the six-membered cyclic ketal from acetone and glycerol, VII, which has not as yet been obtained.[24] It is true that the type of six-membered ring indicated by Formula VII has already been obtained in the condensation of acetone with 1,3-propanediol,[25a] dihydroxyacetone,[25b] penta-erythritol[25c] and xylose,[19] but it was thought that its labile character in Compound VII, with its adjacent free hydroxyl group, might afford an interesting opportunity for studying the effect of methylating reagents when applied to carbohydrates or glucosides containing the equally labile pyranose ring.

The following synthesis suggested itself (Bz=Benzoyl)



V VI VII

Six-membered 1,3-benzylidene glycerol[13c] yields on benzoylation a pure, crystalline 0-benzoate, V, which readily undergoes hydrolysis of its acetal ring under the influence of a trace of acid to yield a glycerol monobenzoate, VI. This should condense with acetone to give a six-membered acetone glycerol benzoate whose ketal ring is considered sufficiently stable toward alkali to withstand the alkaline hydrolysis of the benzoyl group to yield the desired compound, VII.

In carrying out the above scheme, the supposed glycerol 0-benzoate was readily obtained, but in accordance with the advice given by Fischer that monoacyl glycerol derivatives intended for subsequent synthesis should not

---

[22] Pnrdie and Irvine, J. *Chem. Soc., 83,* 1021 (1903).

[23] Haworth, *ibid.,* **107,** 8 (1915).

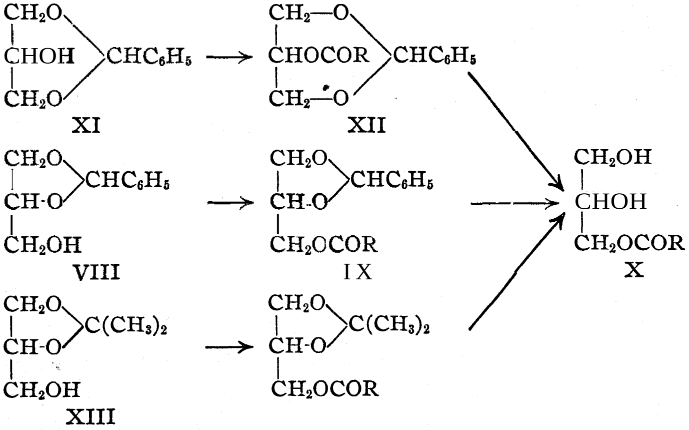
[24] (a) Fischer, Bergmann and Bärwind, *Ber.,* **53,** 1589 (1920); (b) Irvine, Macdonald and Soutar, J. *Chem. Soc.,* **107,** 337 (1915).

[25] (a) Boeseken and Hermans, *Ber.,* **55,** 3758 (1922); (b) Fischer, Taube and Baer, *ibid.,* **60,** 482 (1927); (c) Boeseken, Schaefer and Hermans, *Rec. trav. chim.,* **41,** 722 (1922).

be distilled,[26] no criterion of its purity could be obtained since it would not crystallize. This same compound was recently prepared[14] in an impure, non-crystallizable state by a different method, and was characterized by converting it to the crystalline di-p-nitrobenzoate, which melted at 152–152.5°. A sample of the authors' supposed glycerol β-benzoate was p-nitrobenzoylated according to the procedure described, and in place of the expected glycerol β-benzoate-α,α′-di-*p*-nitrobenzoate (m. p. 152–152.5°), it yielded instead a p-nitrobenzoate melting at 115°, mixed with a small amount of a product with a slightly higher somewhat indefinite melting point. These products were undoubtedly glycerol α-benzoate-β-*p*-nitrobenzoate and glycerol α-benzoate-α,β-di-*p*-nitrobenzoate, melting at 115 and 123°, respectively, as previously recorded by Bergmann, Brand and Dreyer."

It would thus appear that during the hydrolysis of V under **acid** conditions a migration of the *beta*-benzoyl group had taken place, since non-acid media were used in the preparation of V and subsequent *p*-nitrobenzoylation of VI. This tendency of an acyl group to migrate during acid hydrolysis is analogous to that of the change in ring structure of the glycerol cyclic acetal ring itself, brought about under the influence of a trace of dry hydrogen chloride.[13c,d] The solid, crystalline six-membered acetals are in this way converted into an equilibrium mixture of the five- and six-membered isomers.

This wandering of an acyl (benzoyl) group during acid hydrolysis of the cyclic acetal ring was further confirmed in a more rigorous manner, as indicated below



Each of the structurally isomeric benzylidene glycerols VIII and XI was converted under non-acid conditions into a suitable ester of Types IX and XII, respectively. The acetal ring of each was then carefully hydrolyzed

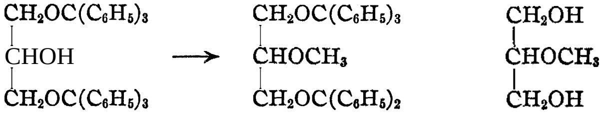
---

[26] Fischer, *Ber.*, 53, 1613 (1920).

so as to leave the newly introduced acyl group intact, resulting in a glycerol mono-ester. Both isomers yielded the same glycerol a-ester, X, indicating that a migration of the *β*-acyl group had taken place between stages XII and X. The identity of the glycerol a-ester was further confirmed by its synthesis from acetone glycerol, XIII, as indicated.

Two parallel sets of experiments were carried out, where R was *p*-nitrophenyl and *p*-bromophenyl, respectively, in order to ensure the presence of crystalline compounds and concomitant strict parallelism in regard to homogeneity at each stage; the benzylidene acetal was chosen on account of its ready ease of hydrolysis. In each case the migration of the acyl group was observed.

Additional proof of the structure of glycerol a-pnitrobenzoate is afforded by its synthesis[27] from a-sodium glyceroxide and p-nitrobenzoyl chloride, as well as from the oxidation of the *p*-nitrobenzoate of allyl alcohol. The recent isolation[28] of glycerol *β*-*p*-nitrobenzoate with a melting point (121°) fourteen degrees higher than its a-isomer should prevent any confusion in the identification of the two isomers. The structure of the intermediate compound, XIV, through which glycerol *β*-*p*-nitrobenzoate was obtained, has been linked up with the authors' investigations of glycerol @-derivatives by the following series of reactions



$$\begin{array}{lcll} CH_2OC(C_6H_5)_3 & & CH_2OC(C_6H_5)_3 & CH_2OH \\ | & & | & | \\ CHOH & \longrightarrow & CHOCH_3 & CHOCH_3 \\ | & & | & | \\ CH_2OC(C_6H_5)_3 & & CH_2OC(C_6H_5)_2 & CH_2OH \end{array}$$

XIV XV

On methylation of glycerol *α,α′*-ditrityl ether, XIV, a crystalline glycerol *α,α′*-ditrityl-*β*-methyl ether, XV, was obtained, from which the two trityl groups were readily removed by hydrobromic acid at 0°, yielding liquid glycerol *β*-methyl ether. The latter compound was then definitely identified by the method described in a previous communication.[29]

The above proof of the migration of *β*-acyl groups in glycerol, as well as that relating to the structure of the cyclic acetals themselves,[13c,d,24b] is based on the non-migration of the ether-linked methyl radical. Although extensive studies have been made on the wandering of alkyl and aryl radicals from carbon to carbon in the pinacolin transformation, and other similar cases[30] are known, the ether-linked alkyl groups seem to possess a very remarkable degree of stability and lack of tendency toward migration.[31] An excellent example of such inertness is afforded by the very recent ob-

---

[27] Fairbourne and Foster, J. *Chem. Soc.,* 127, 2759 (1925); 128, 3146 (1926).

[28] Helferich and Sieber, Z. *physiol. Chem.,* 175, 311 (1928).

[29] Hibbert, Whelen and Carter, THIS JOURNAL, 51, 302 (1929).

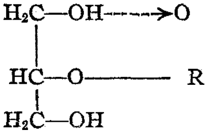
[30] Levy, Bull. *soc. chim.,* 33, 1655 (1923); see also Cohen, "Organic Chemistry," Part II, Edward Arnold and Co., London, 1924, p. 377.

[31] Hirst and Smith, J. *Chem. Soc.,* 1928, 3149.

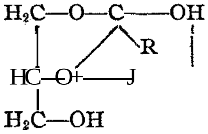
servation in this Laboratory[32] that the vinyl ether of glycol, $CH_2=CHOCH_2CH_2OH$, under the influence of a trace of hydrogen ion undergoes a molecular rearrangement with explosive violence, to form ethylidene glycol, the change involving a migration of the hydroxyl hydrogen atom. On the other hand, the corresponding vinyl methyl ether is quite stable under both acid and alkaline conditions.[33]

Mechanism of the Change Involved in the Migration of Acyl Groups

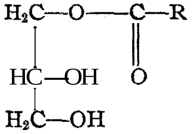
If the spatial configuration and nature of the polarities of the various groupings present in a glycerol β-derivative of Type XVI be considered, it is reasonable to assume that the strongly negative carbonyl group must have a strong affinity for the hydrogen atom of the a-hydroxyl group, resulting in the formation, under the catalytic influence of hydrogen ion, of the intermediate, unstable, five-membered cyclic acetal ring, XVII, postulated by Fischer.[8]



XVI



XVII



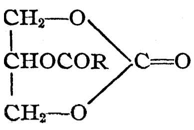
XVIII

This can then undergo ring scission, and with accompanying migration of the hydrogen atom in question, yield the a-derivative, XVIII. The cause of the "tendency toward migration" would seem to be the fact that the energy relations in glycerol derivatives seem best satisfied when the primary alcoholic groups are interacting. In agreement with this idea the ready formation of α,α′-derivatives from glycerol a-derivatives, such as the chlorohydrins, trityl ethers, sodium glyceroxides and others may be noted. If this theory be correct, then the more positive the substituent, R, the less should be the tendency toward migration. Thus the β-trichloro-acetyl group might be expected to wander readily; the β-trimethylacetyl group only with difficulty or not at

---

[32] Hill, This Journal, 50, 2725 (1928).

[33] It is proposed, having in mind the recent work of Haworth[19] on the sugar carbonates, to attempt the synthesis of a compound of the type shown. The ring of such a compound undergoes scission by the action of alkalies, and it will be of interest to ascertain if, under these alkaline conditions, migration of the acyl group from the β- to the α-position takes place.



[34] The possibility of isolating the intermediate compound, XVII, is at present under investigation in these Laboratories. Thus the condensation of methyl formate with glycerol might be expected to yield a stable derivative with the same ring structure as shown in Formula XVII (where R represents hydrogen). Hydrolysis of the methyl group should then lead to ring scission with simultaneous formation of glycerol *a*-monoformate. On the other hand, condensation of glycerol with carbonyl chloride, followed by catalytic reduction of the carbonyl group to a secondary alcohol, would

Conclusion

The experimental evidence submitted clearly indicates that in any operation where the acyl esters of tri- or poly-hydroxy compounds are subjected to acid conditions, great care is necessary in drawing any conclusions as to the constitution of the resulting compounds. It is equally true that conclusions regarding the structure of polysaccharides and carbohydrates drawn from a consideration of the structure of their acylated derivatives must also be regarded with suspicion. If, in addition to this, the remarkable ease of change in such ring structures is recalled, it is evident that great care is necessary in drawing conclusions from either acylation or methylation experiments, especially when there is any possibility of the latter having been carried out in the presence of a slight hydrogen-ion concentration, as advocated by certain workers.[35]

Experimental Part

The first two reactions described below for the attempted synthesis of 1,3-isopropylidene glycerol (2,2-dimethyl-5-*m*-dioxanol) follow the procedure adopted in a former investigation of the benzylidene glycerols,[13c] except for some slight modifications which considerably increase the yields.

Condensation of Benzaldehyde with Glycerol.—One hundred g. of benzaldehyde and 88.5 g. of glycerol (1% excess over the theoretical amount) were placed in a 300-cc. Claisen distillation flask and five drops of concd. hydrochloric acid added. The mixture was then heated to 85–90° at 60–70 mm., that is, sufficiently high to allow the water produced in the condensation to distil off with a minimum loss of unchanged benzaldehyde. In twenty minutes the reaction was complete, as evidenced by the non-separation of two layers when the flask was cooled to 10°. The condensation product was diluted with half its volume of ether and then well shaken with 800 cc. of a 1% solution of potassium carbonate to remove the acid catalyst and any remaining glycerol. The ether solution, without further washing, was dried over fused potassium carbonate and the ether removed by gentle heating under diminished pressure, leaving a mixture of the isomeric 1,2- and 1,3-benzylidene glycerols as a slightly viscous, yellowish oil; yield, 150.5 g. (87%). A solution (saturated at 30°) of this oil in a mixture of ligroin (b. p. 80–90°) and benzene in the proportion of 4:3, deposited the 1,3-isomer as white, fine, silky needles which acted much like wet absorbent cotton when being removed from the flask for filtration. The oily 1,2-benzylidene glycerol (2-phenyl-1,3-dioxolane-4-carbinol) remains dissolved in the mother liquor. The 1,3-benzylidene glycerol (2-phenyl-5-m-dioxanol) after recrystallization from ether at −10° melted at 83°, in agreement with that of previous preparations.

---

yield Compound XVII (where R represents hydrogen) directly, which would presumably then undergo a similar transformation to glycerol a-monoformate under the influence of an acid. A third, more direct, method is based on the observation by Tanasescu [*Bull. Soc. stiinte cluj*, 2,369 (1925)] that o-nitrobenzylidene gylcol undergoes a re-arrangement in direct sunlight, to 2-*o*-nitrosophenyl-2-hydroxy-1,3-dioxolane, which contains the same type of configuration as Compound XVII. Preliminary experiments with the corresponding glycerol derivatives are in progress.

[35] Haworth, "Constitution of the Sugars," Edward Arnold and Co., London, 1929, p. 55.

Preparation of **1,3-Benzylidene** Glycerol 2-Benzoate (2-Phenyl-5-m-dioxanol Benzoate).—Twenty g. of crystalline 1,3-benzylidene glycerol was dissolved in *25* g. of dry pyridine and a solution of 18 g. of benzoyl chloride in 15 g. of dry pyridine added, with constant stirring. The heat of reaction was slowly allowed to dissipate, after which the mixture stood for forty-eight hours at 18°. The semi-liquid product was poured into one liter of cold water, causing the separation of a mass of crystalline granules which were washed with water and dried at 60° under reduced pressure. Recrystallization from 300 cc. of a saturated, boiling ether solution yielded the pure benzoate as large, colorless, prismatic needles melting at 103°. Evaporation of the mother liquor to 100 cc. and cooling to −10° yielded a second crop with m. p. 99–100°. Total yield, 29 g. (93%).

Hydrolysis of **1,3-Benzylidene** Glycerol 2-Benzoate to Glycerol **Monobenzoate.**—Twenty g. of the benzoate was allowed to simmer in an open beaker at 80° for thirty minutes with 200 cc. of a 50% aqueous solution of ethyl alcohol containing 0.5 cc. of concd. hydrochloric acid. Benzaldehyde was freely evolved. After careful neutralization with 10% potassium carbonate, the alcohol, water and remaining benzaldehyde were removed by heating under diminished pressure and the residue was extracted from the inorganic salts with 150 cc. of ether. Drying over calcium chloride, followed by removal of the solvent, left 8 g. of a slightly brown, viscous oil which could not be induced to crystallize; yield, 60%. It was redistilled for the following experiments.

Identification of the Supposed Glycerol **β-Benzoate.**—One g. of the distilled oil, dissolved in 5 g. of dry pyridine, was added to a solution of 1.9 g. (two equivalents) of *p*-nitrobenzoyl chloride in 12 g. of dry pyridine. After standing for twenty-four hours at 18° the reaction mixture was poured into 400 cc. of cold water, which caused the separation of a gummy, yellowish mass. Upon vigorous stirring with fresh quantities of water, the product slowly became almost solid and was taken up in 50 cc. of chloroform, washed with cold, saturated potassium bisulfate and sodium bicarbonate solutions, then dried over fused potassium carbonate. Upon dilution of the chloroform solution with petroleum ether until it was cloudy at room temperature, then cooling slowly to −10°, a few small, white, nodular aggregates with indefinite m. p. 119–121° separated, followed by a deposit of straw-colored clusters of microscopic needles melting sharply at 115". The amount of the higher-melting compound did not permit of further recrystallization, but its melting point corresponds closely to that of glycerol α-benzoate-α′,β-di-*p*-nitrobenzoate (123°), while the lower-melting compound was evidently glycerol α-benzoate-β-*p*-nitrobenzoate.[6] Analyses were not made.

p-Nitrobenzoylation *of* **1,3-Benzylidene** Glycerol.—Two g. of 1,3-benzylidene glycerol was dissolved in *5* g. of dry pyridine and added to a solution of 2 g. of *p*-nitrobenzoyl chloride (slightly less than one equivalent, to avoid possible formation of *p*-nitrobenzoic anhydride)[36] in 10 g. of dry pyridine. The mixture was allowed to stand for fifteen hours at 30° and then poured into 400 cc. of cold water. The flocculent, pale yellow material which separated out on stirring was taken up in 50 cc. of chloroform, the solution washed with cold saturated potassium bisulfate and sodium bicarbonate solutions, and dried over fused potassium carbonate. Removal of the solvent left a crystalline mass which on recrystallization from ethyl acetate by cooling to —10" yielded 2 g. of straw-colored clusters of prisms. This compound, 1,3-benzylidene glycerol-2-p-nitrobenzoate (2-phenyl-5-m-dioxanol-p-nitrobenzoate), melts sharply at 156° and is apparently a new derivative. It is soluble in most organic solvents except alcohol, petroleum ether and ligroin and is insoluble in water.

Anal. Calcd. for $C_{17}H_{15}O_6N$: N, 4.25. Found (Micro-Dumas): 4.12, 4.38.

p-Nitrobenzoylation of **1,2-Benzylidene** Glycerol.—Thirteen and one-half g. of the

---

[36] See in this connection, Stather, ***Ber.***, 57, 1392 (1924).

1,2-benzylidene glycerol recovered from the benzene–ligroin mother liquor in the condensation of benzaldehyde and glycerol previously described, and which had been distilled within the range prescribed in a previous communication,[13e] was treated with 13.3 *g.* (slightly less than one equivalent) of *p*-nitrobenzoyl chloride in exactly the same manner as its 1,3-isomer. Upon cooling the ethyl acetate solution of the crude product, 3 g. of the isomer melting at 156° was obtained, identical with that obtained in the previous experiment.''' The solvent was removed from the mother liquor under reduced pressure and replaced by an acetone–alcohol mixture of approximately equal parts by volume which, by cooling to −10° and slowly adding water, a few drops at a time with shaking, yielded 8.3 g. of yellowish crystals with a very indefinite m. p. of 80–90". A small sample, recrystallized from acetone, gave only a minute quantity of white nodules[38] melting at 190–191°. The purification of the remaining product was effected by extraction with benzene, in which this high-melting impurity was found to be relatively insoluble. The extract, upon dilution with petroleum ether to the point of cloudiness at 0°, gave on long standing at −15° almost colorless crystals melting indefinitely between 84 and 90°. By further recrystallizations from ethyl acetate–petroleum ether at −15°, 5 g. of straw-colored needles melting at 90–91° was eventually obtained. This compound, 1,2-benzylidene glycerol-3-p-nitrobenzoate (2-phenyl-1,3-dioxolane-4-carbinol-*p*-nitrobenzoate), is apparently not recorded in the literature. The solubilities of this compound are similar to those of its isomer.

Anal. Calcd. for $C_{17}H_{15}O_6N$: N, 4.25. Found (Micro-Dumas): 4.28, 4.42.

Acid Hydrolysis of the Isomeric Benzylidene Glycerol *p*-Nitrobenzoates.—One *g.* of each of the isomers was dissolved in 10 cc. of ethyl alcohol, then diluted with an equal volume of water to which 0.5 g. of concd. hydrochloric acid had been added. The milky solution was allowed to simmer in an open Erlenmeyer flask for twenty minutes, during which time benzaldehyde was continually evolved. The solution was then evaporated almost to dryness under reduced pressure, neutralized exactly with 10% potassium hydroxide and the evaporation carried to dryness under 10-mm. pressure. The sirupy residue was separated from inorganic salts by extraction with 20 cc. of ethyl acetate, the solution after filtration diluted with petroleum ether to the point of cloudiness at 0° and then further cooled to −15°. Unless considerable care was exercised, the compound, despite its m. p. of 107°, tended to come out as an oil even at −15°. After a seeding crystal had once been obtained, beautiful crystals melting at 106.5' could be grown readily. In each case, the product proved to be identical with a sample of glycerol α-*p*-nitrobenzoate prepared from acetone-glycerol-p-nitrobenzoate following the procedure given by Fischer.[24a] A mixed melting-point determination of all three melted at 106–106.5°. Since in both cases an a-derivative resulted, a migration of the β-acyl group during the hydrolysis of 1,3-benzylidene glycerol-2-p-nitrobenzoateis indicated.

The various *p-bromo*benzoates were prepared by methods exactly analogous to those just described for the *p-nitro*benzoates. These compounds all possessed a considerable tendency to separate from solvents as oils until seeding crystals had been prepared, when beautifully crystalline, colorless

---

[37] This indicated that the original distilled compound contained at least 12% of the isomeric 1,3-benzylidene glycerol held in solution. This same impracticability of completely separating the two isomers by distillation was noted in previous preparation~'~of their methyl ethers.

[38] This compound is probably *p*-nitrobenzoic anhydride, although the possibility of the formation of glycerol tri-p-nitrobenzoate (m. p. 192") from traces of glycerol in the distilled original compound is not excluded.

compounds could usually be obtained, all of which are apparently new derivatives.

1,3-Benzylidene-glycerol-2-*p*-bromobenzoate (2-phenyl-5-*m*-dioxanol-*p*-bromobenzoate) was prepared from 2 g. of 1,3-benzylidene glycerol and a pyridine solution of 2.5 g. of *p*-bromobenzoyl chloride, in 80% yield. Recrystallization from 20 cc. of warm ethyl acetate gave colorless needles melting at 146°, soluble in chloroform, ether, benzene; insoluble in petroleum ether, ligroin, alcohol and water.

Anal. Subs., 9.150, 9.798: AgBr, 4.763, 5.166. Calcd. for $C_{17}H_{15}O_4Br$: Br, 22.01. Found: 22.15, 22.44.

1,2-Benzylidene-glycerol-3-*p*-bromobenzoate (2-phenyl-1,3-dioxolane-4-carbinol-p-bromobenzoate), isomeric with the above, was prepared from 1.7 g. of the impure, liquid 1,2-benzylidene glycerol and a pyridine solution of 2 g. of p-bromobenzoyl chloride. As expected, the product was contaminated with its higher-melting isomer. Successive recrystallizations from (a) hot methyl alcohol and (b) ethyl acetate–petroleum ether (1:2) finally yielded large, colorless crystals melting at 72°, which had a peculiar, greasy consistency when cut. These were soluble in most organic solvents except cold alcohol, petroleum ether and ligroin; insoluble in water.

Anal. Subs., 9.087, 8.920: AgBr, 4.695, 4.571. Calcd. for $C_{17}H_{15}O_4Br$: Br, 22.01. Found: 21.99, 21.81.

Acetone-glycerol-α-*p*-bromobenzoate (2,2-dimethyl-1,3-dioxolane-4-carbinol-*p*-bromobenzoate) was prepared from 2.5 g. of acetone-glycerol and 4.2 g. of *p*-bromobenzoyl chloride in pyridine solution. The colorless oil remaining after evaporation of the solvent from the chloroform solution of the reaction product was heated to 100° for a few minutes under 0.5 mm. to remove the last traces of solvent. After standing at 18° for three days, two small crystals had formed. Subsequent recrystallization from warm petroleum ether of the solid mass obtained with the aid of these seeding crystals yielded small, colorless needles melting at 39-40', soluble in most organic solvents except cold petroleum ether and low-boiling ligroin, and very prone to separate as an oil during crystallization; yield, 70%.

Anal. Subs., 8.551, 8.792: AgBr, 5.06 6,5.228. Calcd. for $C_{13}H_{15}O_4Br$: Br, 25.36. Faund: 25.21, 25.30.

Acid hydrolysis of small samples of each of the three compounds last described was carried out in exactly the same manner as with the corresponding *p*-nitrobenzoates, and yielded three identical specimens of glycerol-a-p-bromobenzoate, as shown by a mixed-melting point of 68-69 °. Since an a-derivative resulted in each case, a migration of a β-acyl group is again indicated during the hydrolysis of 1,3-benzylidene-glycerol-2-*p*-bromobenzoate.

Glycerol-a-p-bromobenzoate, apparently not hitherto described in the literature, was obtained on recrystallization from warm benzene as small clusters of transparent needles, m. p. 70°. Crystallization is only induced with difficulty, most readily by scratching a small sample of the oily form immersed in petroleum ether. It is soluble in most organic solvents except cold ether, benzene, petroleum ether and ligroin; insoluble in water.

Anal. Subs., 8.994, 8.435: AgBr, 5.983, 5.701. Calcd. for $C_{10}H_{11}O_4Br$: Br, 29.02. Found: 28.31, 28.77.

Preparation of Glycerol-α,α′-ditrityl-β-methyl Ether. **XV.**—Fifty g. of glycerol-α,α′-ditrityl ether, XIV, prepared by the method of Helferich and Sieber[28] (m. p.

175–176°; yield, 86%) was dissolved in a mixture of 80 cc. of benzene and 50 g. of methyl iodide and methylated in the usual manner by the slow addition, with constant stirring, of 40 g. of dry silver oxide during a period of three hours, during which the temperature was raised to 50°. The heating and stirring were continued for a further period of eight hours. The reaction mixture was filtered with suction and to the filtrate were added two warm benzene extractions of the silver oxide–silver chloride residue. The total filtrate was then evaporated under reduced pressure to a volume of 75 cc. and on cooling 38 g. of a white amorphous powder separated. Further evaporation and cooling of the mother liquor gave 11.7 g. of the same material. Recrystallization from hot ethyl acetate yielded large, colorless crystals of glycerol-α,α'-ditrityl-β-methyl ether, melting sharply at 158.5°. This compound, soluble in ethyl acetate, benzene, chloroform and ethylene bromide, insoluble in ether, ligroin and water, has not been previously described in the literature; yield, 49.7 g. (97%).

Hydrolysis of Glycerol-α,α'-ditrityl-β-methyl Ether, XV, to Glycerol–&methyl Ether.——Forty-three g. of glycerol-α,α'-ditrityl-β-methyl ether was dissolved in 100 cc. of an 80% solution of glacial acetic acid in benzene and cooled to 0°. Slow addition of 30 cc. of a cold, saturated solution of hydrogen bromide in glacial acetic acid caused immediate precipitation of trityl bromide, which was filtered off and sucked as dry as possible. The filtrate was neutralized with dry potassium carbonate and heated under reduced pressure to remove the bulk of the benzene and the water formed in the neutralization. The extremely bulky, frothy suspension of potassium acetate was extracted three times with a total of 150 cc. of acetone, which was then dried over calcium chloride and evaporated to a volume of 25 cc., resulting in the deposition of 3.5 g. of triphenylcarbinol (formed by hydrolysis of trityl bromide). After filtration, the acetone solution of the glycerol β-methyl ether was distilled under reduced pressure. The acetone readily evaporated and as the bath temperature was gradually raised to 150°, 1.5 g. of a colorless liquid was collected between 118–140° at 13 mm., leaving **a** residue of 1.5 g. of solid triphenylcarbinol in the flask. The wide range of temperature (glycerol-β-methyl ether has a b. p. of 123" at 13 mm.) is explained by the fact that considerable superheating was necessary to distil the ether from the unavoidable residue of solid triphenylcarbinol; yield, 19%.[39] For the positive identification[z9] of the distillate, **a** portion was condensed with p-nitrobenzaldehyde and yielded 0.9 g. of 1,3-*p*-nitrobenzylidene glycerol-2-methyl ether (2-*p*-nitrophenyl-5-*m*-dioxanol methyl ether), m. p. 138°, with no trace of the isomeric α-ether derivative.

Summary

1. A review of the literature shows that the β-acyl group in glycerol derivatives readily undergoes migration to the a-position.

2. The mechanism of such migration is apparently that first proposed by E. Fischer, namely, the intermediate formation of an unstable cyclic acetal. Three methods are suggested for the synthesis of the latter product.

3. There does not appear to be any reliable evidence in the literature indicating the migration of a methyl or other alkyl group, in the case of glycerol and other alkyl ethers.

4. Experimental evidence is given proving that in the hydrolysis of various β-acyl derivatives of glycerol cyclic acetals, a migration of the acyl

---

[39] This experiment is being repeated in an effort to perfect a more satisfactory procedure for the isolation of the glycerol β-methyl ether from the strongly acid hydrolysis mixture.

radical from the β- to the a-position takes place, giving as final product an α-glycerol ester.

5. The data submitted provide further convincing evidence as to the unreliability of deductions relating to the structure of glycerol, carbohydrates and polysaccharides based on conclusions drawn from experiments on the hydrolysis of their acyl derivatives.

MONTREAL, CANADA

NEW BOOKS

The Origins and **the** Growth **of** Chemical Science. BY J. E. MARSH, M.A., F.R.S., Fellow of Merton College. John Murray, 50A Albemarle Street, London, W. 1, England, 1929. x + 161 pp. Illustrated. 12.5 X 19 cm. Price, 5 **shillings,** net.

The history of chemistry, from the point of view of the author of this small but compact and well-filled book, is not a mere record of events. The events must be interpreted, correlated, put in order—for history itself is also a science and its data, however interesting they may be in themselves as data, still submit to a scientific treatment. Marsh interprets the history of chemistry as the history of two principal ideas—of the idea of salt formation, first clearly articulate with Boyle and even now presenting problems and influencing research, and of the idea of the fixation of gases, with the early work on which the names of Black, Priestley, Cavendish, Scheele and Lavoisier are associated.

In his preface Marsh says that "there was no science of Chemistry before the seventeenth century, but the art of Chemistry had progressed through long ages," etc. His first chapter is devoted to the "fire theories" of the ancient philosophers and of the alchemists and phlogistonists. Now it seems to the reviewer that, where we have theories, there we have data interpreted—and have science. Primitive chemical theories were chemical theories after all, not wilfully fantastic perversions of thought. We wish to know how they came to be and the reasons which led to their abandonment. Marsh points out that the phlogiston doctrine, which was the last stand of the ancient fire theory, was put forward in 1702 but "did not attract much attention from chemists in Stahl's lifetime or for some forty years after his death in 1734. The theory was then taken up by Priestley, by Scheele and by Cavendish, to explain the nature of the gases which they discovered." But the quantitative phenomena connected with the fixation of gases showed its inadequacy and created the necessity for the interpretations of Lavoisier.

The book contains a number of things such, for example, as the mention of Higgins's suggestions in 1789 relative to multiple proportions, which show that the author has a scholarly knowledge of his subject. One chapter details briefly the essential facts about the discovery of each of the known elements. The index is excellent and the names of men are generally followed by dates and often by a mention of a biography. Students will find that the book arouses their interest in the history of chemistry. Those who are already familiar with the subject will find it refreshingly different and will perhaps question, as the reviewer has done, whether the text has not determined the argument, whether the motives which run through the unfolding drama of chemistry are not more involved and far more numerous than Marsh's book would lead one to think. Yet Marsh has made an excellent study of two of these motives.

TENNEY L. DAVIS

Chemisches Fachwörterbuch für wissenschaft Technik, Industrie und Handel. (Chemical Dictionary for Science, Industry and Business.) Edited by A. W. MAYER. Otto Spamer, Leipzig, Germany, 1929. Vol. I. German–English–French. 826 pp. Price, unbound, M. 70; bound, M. 75.

A review of so complete and voluminous a work as this can cover little more than a certification of its extent, the evident care and efficiency of its production and the very complete field it covers. Prepared by one who has had special experience in translating, it really does cover more than a mere list of German technical words with their English and French equivalents, but while serving as a very complete scientific chemical dictionary, it "simultaneously introduces practical examples of the chemical and chemico-technical phraseology customary for the several industries in the three principal languages" and gives "special consideration to the requirements of trade and of the industrial and technical expert by giving appropriate equivalents, in the languages concerned, for the special professional terms and phrases for manufacturing processes, special machinery, apparatus, etc." The second volume which is to follow will be in English–French–German, and the third in French-German–English. Those who are fortunate enough to have this volume in their libraries should have no difficulty in obtaining the correct English or French equivalent for almost any German word or technical phrase.

CHARLES L. PARSONS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. IX. Arsenic, Antimony, Bismuth, Vanadium, Columbium and Tantalum. By J. W. MELLOR, D.Sc. Longmans, Green and Company, 55 Fifth Avenue, New York; 1929. xiv + 969 pp. 113 figs. 25 × 16 cm. Price, $20.00.

The publication of this valuable handbook is progressing with commendable rapidity. The present volume exhibits the same treatment and embodies the same excellent qualities as the earlier volumes. Here as before the author has succeeded in making at once succinct and readable what is essentially and unavoidably an encyclopedia.

ARTHUR B. LAMB

Volumetric Analysis. Volume I. The Theoretical Principles of Volumetric Analysis. By DR. I. M. KOLTHOFF, Professor of Analytical Chemistry, University of Minnesota, with the collaboration of Dr. ING. H. MENZEL, Dresden, Germany. Translated from the German by N. Howell Furman, Associate Professor of Analytical Chemistry, Princeton University. John Wiley and Sons, Inc., New York, 1928. xvii + 289 pp. 20 figs. 15.5 × 23.5 cm. Price, $3.00.

Ostwald, in 1894, wrote an interesting little book showing some applications of physical chemistry to analytical chemistry and his ideas have been carried farther by Bottger, A. A. Noyes, Stieglitz, W. M. Clark, Erich Müller, Kolthoff and others. In fact, most teachers of analytical chemistry now believe that it is more important to stress the underlying theories rather than the laboratory procedure and have found that students actually do better work in the laboratory when they understand what they are doing rather than follow procedures blindly. The purpose of this new book by Kolthoff is to explain the reactions of analytical chemistry in terms of the mass-action law. From this principle it is possible to predict whether a reaction is suitable for quantitative work, to calculate the titration error on the assumption that the observations are correct and to determine the ideal conditions for carrying out an analysis. The book, therefore, is a welcome addition to the literature of analytical chemistry.

There is probably no one living today who has contributed so much to the scientific study of volumetric analysis; Kolthoff publishes about twenty-five papers a year, all of them having merit. A considerable part of this book has, therefore, been published already in his scientific papers. It is well to have the subject matter collected and published again.

It is undeniably wrong to teach chemical theory entirely apart from chemical practice and it is far better to teach physical chemistry to Freshmen and to Sophomores than to wait till the Junior or Senior year before attempting to discuss in detail the theories underlying all chemical work. Theory helps one to remember and correlate facts and the Freshman who is ready to study calculus is able to understand the mathematics of science and he has greater respect for both mathematics and science when the relationships are shown early in his career.

There is no mathematical equation given in this book but what is easily understandable by the average college student and there is little, if anything, that ought not to be taught to beginners in analytical chemistry. Equations, such as that of Nernst for showing the relation of electrolyte concentration to electrode potential, and which are derived with the aid of integral calculus, are not explained at all but the student is asked to take them for granted.

On the other hand, it is well known to teachers of chemistry that college students often have considerable difficulty in applying simple arithmetical principles to chemical reasoning and so it is necessary, in order to accomplish the best results, to introduce mathematical equations cautiously at first and with considerable explanation, seemingly unnecessary to the mathematical expert. In this way, Stieglitz and Clark have written books which are instructive and based on mathematical reasoning but are at the same time intensely interesting. The book under review was not written with this idea in mind; it will be read and understood easily only by one who is thoroughly conversant with the mathematical nomenclature of physical chemistry. Thus on page 245, the usual method of expressing concentrations in volumetric analysis is discussed at some length (something that every student of analytical chemistry is taught at the start) but throughout the preceding pages of the book concentrations are invariably expressed in moles per liter without any comment because this is something that every student of physical chemistry is supposed to know.

Chapter I is particularly difficult for the beginner; 107 numbered equations are given in 42 pages of text. This makes hard reading and unless one is familiar with the conventional terms of physical chemistry it is difficult to see exactly what some of the unexplained equations really mean. Thus on page 2, the idea of Sorensen's "ion exponent" is introduced and thereafter low concentrations are usually expressed in terms of negative logarithms. So instead of saying that the solubility product, S, of calcium carbonate is 1.2 X 10^{-8}, the expression $p_S = 7.92$ is advocated. This is all very well but it would almost seem as if more explanation should be given. To illustrate the extent to which the mathematical development has gone, it may be mentioned that pages 31 and 32 are devoted to the calculation of the extent to which calcium carbonate is hydrolyzed in pure water on the basis of the ionization constant of water and the secondary ionization constant of carbonic acid. This involves the solving of a cubic equation. Unfortunately, Kolthoff has used here a value for the ionization of carbonic acid which is ten times as large as the value he gives on page 276 and which is presumably correct.

The work of the translater is well done; the English is good and the meaning is clear, although at times the translation is a little too literal.

Without going into further details, the reviewer wishes to emphasize the fact that this is a good book and well worthy of publication. It is to be hoped, however, that both Kolthoff and Furman will try the experiment of teaching this sort of thing to beginners and then after a few years they will amplify and modify the book so that it will be easier reading.

WILLIAM T. HALL

Messen und Wägen, ein Lehr- und Handbuch insbesondere für Chemiker. (Measurement and Weighing. A Text and Handbook Especially for Chemists.) By Dr. WALTER BLOCK. Otto Spamer, Heinrichstrasse 9, Leipzig, Germany, 1928. viii + 339 pp. 109 figs. 17.5 × 25 cm. Price, unbound, R. M. 25; bound, R. M. 28.

In this volume the author carries out a project originally planned by Dr. Fritz Plato, director of the Reichsanstalt für Mass- und Gewicht, who has supplied the first section. This section (48 pages) deals with historical notes, with the units and fundamental standards of the metric system, with the British Imperial units and with the differences between these and the "customary" units of the United States. This is followed by valuable notes on the care and handling of standards, and on the various standard temperatures in use.

The second section (**32** pages) discusses the number of figures to retain in computations, the computation of "mean error" and of "probable error," the distribution of errors among the various measurements of a determination and simple approximation formulas for small correction and reduction factors. Nearly five pages are devoted to slide rules, computing machines, monographic charts and tables used in computation.

In the third section (**13** pages), are given what may best be called explanations of the fundamental units of mass, length, time, force, work, energy and pressure, with the standard value of gravity; then short definitions, with dimensional equations, of the units of the c. g. s. system, and a discussion of the most important physical constants—chiefly those of interest to the chemist.

The remaining three-fourths of the book deals directly with the various kinds of measurements, divided as follows: Time, 6 pages; Angle, 7 pages; Length, 25 pages; Surface, 4 pages; Volume and Capacity, 28 pages; Weighing, 22 pages; Density, **37** pages; Pressure, **14** pages; Humidity, **3** pages; Temperature, **29** pages; Heat (quantity), 7 pages; Photometry, 5 pages; Optics (refraction, interference, polarimetry), 14 pages; and Electrical Measurements, **38** pages.

There is also a classified list of over 200 references. In such a list it seems strange to miss the International Critical Tables. It also seems strange to find the Technological and the Scientific Papers of the Bureau of Standards classed as magazines devoted chiefly to methods of measurement.

An outstanding feature of the book is the careful explanation of principles involved. These give usable concepts rather than mere definitions or facts, and many items that tend to a broader culture than is likely to be gained from many mere "reference books."

A number of omissions are no doubt debatable, but some seem strange. For example, neither the Michaelson nor the Abbé-Fizeau interferometers are mentioned in connection with interference measurements; also the dew point instrument is not mentioned, nor are any methods of controlling humidity given.

On page 150 the emphasis on "relative" weighing, as opposed to finding values in correct units of mass, seems very unfortunate.

In the section on humidity, the author speaks of the amount of water vapor that *the air can take* up, thus continuing the old error. Later, a hair hygrometer is said to be checked by checking the saturation point, with no mention of any need for checking some other point also. Neither is there any mention of the fact that checking the **100%** point is likely to cause serious changes in reading for many days in the future.

The discussion of standard weights on pages 150 to **152** is greatly complicated, for American readers especially, by the inclusion of ordinary commercial standards. "Prazisionsgewichte," for which tolerances are given, are not laboratory weights. In fact there are *no* German tolerances for laboratory weights.

On page 44, and again on page **151,** it is stated that quartz weights are not suitable for precise standards because of the variable moisture film on the surface. Yet researches on adsorption show quartz to have as little as or less than the amount on highly polished metal.

In a book covering so wide a range of topics and such a large amount of detail, one can hardly avoid overlooking many points worth mentioning; and in the present case the reviewer must admit having given scant attention to the sections on electricity and heat, particularly. Neither was any special attention given to checking the accuracy of details, but the examples above show that caution must be exercised in using the book.

A. T. PIENKOWSKY

The Determination of Hydrogen Ions. By WILLIAM MANSFIELD CLARK, Ph.D., Professor of Physiological Chemistry, The Johns Hopkins University. Thiid edition. The Williams and Wilkins Company, Baltimore, 1928. xvi + 717 pp. 100 figs., 1 plate. 15.5 X 23.5 cm. Price, $6.50.

Clark's book since the appearance of its first edition in **1920** has been the standard on its subject. The new edition brings it abreast of the moment in its rapidly developing field. There are several entirely new chapters. New techniques are described, including the application of spectroscopy and colorimetry, and of metallic oxide, glass and oxygen electrodes. The theoretical treatment is broadened by chapters on the theory of titration, on changes of free energy and on the Debye-Hückel extension of Arrhenius' dissociation theory. Many chapters represented in the previous edition have been so completely revised that they constitute largely new material. The chapter on oxidation–reduction potentials has been nearly doubled to include new developments of the field, due in no small part to Clark's own investigations. The author has adhered to a style as condensed as is consistent with clarity. The precise choice of words gives continual satisfaction. The expansion of the entire book from the 480 pages in the second edition has been forced, despite the condensed form, by the new material demanding presentation. The printer's work is well done.

DONALD D. VAN SLYKE

Molecular Rearrangements. By C. W. PORTER, Professor of Chemistry, University of California. The Chemical Catalog Co., New York City, 1928. 167 pp. 16 × 23.5 cm. Price, $4.00.

The subject of molecular rearrangements is the family skeleton in the organic chemist's closet. Everyone knows that rearrangements occur but one is rather loath to talk about them. If they were the rule rather than the exception, organic chemistry would be a nightmare. As it is, the possibility of a molecular rearrangement haunts every series of transformations and all the pretty "proofs of structure" exhibited to our students should be followed not by the letters Q.E.D. but by B.M.R. (barring molecular rearrangements).

The appearance of Professor Porter's monograph will undoubtably serve to direct the attention of students and teachers to the subject of molecular rearrangements. It is now possible, for the first time, to refer an advanced student to a book dealing with the subject. The bibliography will be of value to investigators who wish to become oriented in regard to the published work on any particular type of rearrangement. The book makes no pretense of being a complete summary of the subject. This choice of a limited amount of material makes it a more readable book than would otherwise be the case and probably many who are not organic chemists will peruse it with interest and enjoyment.

The first four chapters deal with carbon to nitrogen, nitrogen to carbon, carbon to carbon and oxygen to carbon rearrangements. A special chapter is devoted to migrations between oxygen, nitrogen and sulfur, and the two final chapters deal with metatheses and certain reversible processes. There is an interesting preface giving one a glimpse of the author's point of view in regard to the much-debated subject of the mechanism of rearrangements. In this connection it seems strange that there is no discussion in the book of Meerwein's work on the mechanism of the Wagner rearrangement. This work seems to the reviewer to be one of the outstanding developments in the last ten years and to provide the experimental basis for a discussion of the mechanism of a large class of rearrangements.

JAMES B. CONANT

Organic Chemistry. A Brief Introductory Course. By JAMES BRYANT CONANT, Professor of Chemistry, Harvard University. The Macmillan Company, New York, 1928. ix + 291 pp. 30 figs. 14.5 × 22 cm. Price, $2.65.

This is an excellent book, designed for the shorter courses in organic chemistry. There is no text of its size which equals it, in the opinion of the reviewer. In fact, many larger books could be cited which fail to present an equally adequate idea of organic chemistry, its relations to other disciplines and to industry. In his preface, the author states that the book was planned to arouse an interest in the subject, as the first necessity in teaching it. On the testimony of students, the book is interesting—on the testimony of the reviewer, it is interesting, even after much reading of organic texts.

There are several points about the book which are worth some amount of discussion. Probably the most important one is the radical departure from the time-honored start-off with the saturated hydrocarbons. Whether this is an advantage or not is difficult to decide, since it is impossible to apply the experimental method! In the reviewer's opinion, there is a loss to be faced, in starting with the alcohols, which is not counterbalanced by the facility with which the student's interest may be seized, or the ready material for treating isomerism for the first time. With regard to the latter point, it must be admitted that it is easier to see differences in the formulas with an O in them, than in those containing only C's and H's. At any rate, the first chapter is most deftly handled, and will repay study by all who are interested in teaching organic chemistry, regardless of their predilections.

Another minor issue to be joined, is the amount of space which should be granted to the benzenoid–quinoid relationships, even in a text of this size. One is rather led to suspect that Dr. Conant has unduly limited himself in this discussion, through a desire to avoid over-emphasis of a field in which he is so effectively interested.

Perhaps it is time to mention the two points which have most impressed the reviewer. The first is the very great amount of information which has been compressed into a small compass, without any perceptible slackening of the even flow of the author's notable style. The book will require study, but it will be easy to study. The second point is the nice degree of emphasis which has been placed on industrial processes. Most texts, even much larger ones, leave much to be desired in this respect, either through the inadequacy of the space assigned to industrial processes, or through lack of up-to-dateness. It is certain that the latter fault does not appear here, in the cases of which the reviewer has personal knowledge.

All in all, this is not just one more organic text, but a new text, of considerable pedagogic importance, and it should be a success. The publishers have done their part well. The drawings are beautifully executed.

W. H. HUNTER

Das Anthracen und die Anthrachinone, mit den zugehörigen vielkernigen Systemen. (Anthracene and Anthraquinones, and their Polynuclear Systems.) BY DR. J. HOUBEN, Professor at the University of Berlin, with the cooperation of Dr. Walter Fischer. Georg Thieme, Antonstrasse 15/19, Leipzig C 1, Germany, 1929. xxiii + 890 pp. 17 X 25.5 cm. Price, unbound, M. 85; bound, M. 90.

In the introduction to this comprehensive treatise, Professor Houben states that he began collecting material for such a book over twenty-five years ago, when he was at the beginning of a period of experimental activity in the field of anthraquinone and alizarin chemistry. It is worth while pointing out that it is only because of the rather unusual nature of his association with an industrial firm that Professor Houben's name is little known in this connection, for the value of a book dealing with a phase of chemistry which has been so closely related to the growth of the German dyestuff industry is greatly enhanced by the knowledge that the author brings to the undertaking the authority of many years of collaboration in technical work. The German patent literature affords a source of information concerning anthracene and anthraquinone which is extremely fruitful, but which, because the observations are widely scattered and of unequal reliability, is rather difficult to use. A great service has been performed by Professor Houben in classifying all of this information (to January 1, 1928), in evaluating it in the light of his technical experience, and in combining it in masterly fashion with the material to be found in the non-technical literature.

The book considers first, in a general section, the history, the systems of nomenclature, the structure and the relationship between the structure and the fluorescence of the anthracenes and anthraquinones, while special sections are devoted to the derivatives of anthracene and dianthryl, the quinones, the condensed systems and the radicals of the anthracene series. The anthraquinone dyes are treated fully, though without the inclusion of details relative to the processes of dyeing. The work is characterized by the great care and thoroughness with which the extensive literature has been marshaled and the information systematized. There are over seventy tables summarizing the properties of groups of related compounds, while a useful index to the German patents precedes a very excellent general index. Professor Houben has dealt particularly skilfully with the arrangement of the chapters relating to the very complicated and diverse polynuclear systems; the general properties and methods of preparation of each type of compound are clearly set forth, together with an account of the useful dyestuffs falling within each group.

The book is written in a very clear style, and the reader will derive much satisfaction from the interesting and unhurried accounts of the major investigations of the chemistry of anthracene. The extensive use of full structural formulas and of well-planned diagrams, combined with the beauty of the printing, further adds to the reader's pleasure. There are, for example, no less than 147 formulas illustrative of the principles enunciated in the chapter on the relationship between color and constitution.

A further noteworthy feature of the book is the inclusion of several passages or notes, dealing largely with the technical preparation of alizarin, which were contributed by Professor Iljinsky. The most interesting of these is the account of his discovery of the catalytic action of mercury in the sulfonation of anthraquinone.

Professor Houben's work is not merely an excellent summary of anthracene chemistry, but it also represents a definite addition to this field of knowledge. It is only in this latter aspect that the reviewer can suggest a possible source of criticism, which is that the author has not always succeeded in properly relating the chemistry of anthracene to general chemical theory. On the one hand, the general theory might have been called on more in accounting for phenomena in the special field. Thus the accepted mechanism of the addition of hydrogen chloride and of aniline to quinone might have been applied with profit to the action of these reagents on anthraquinone-azine (pp. 719, 720), and the older mechanism suggested for the Bally benzanthrone synthesis might be revised in the light of the modern view of the ordinary Skraup reaction. Kehrmann's work on the relative oxidation potentials of simple hydroazines [Ber., **31,** 977 (1898)] is perhaps not generally recalled, but it may be said that this work admirably accounts for all of the facts known concerning the relative fastness to chlorine of the indanthrene dyes (p. 729). The reviewer feels that, on the other hand, the opportunity to extend general chemical theory from the facts known about the higher hydrocarbons has not always been utilized fully. The existence of addition products of anthracene with nitric acid and with bromine is surely of significance in connection with the theory of substitution in the benzene ring. Taken by itself, it is difficult to understand the fact that, of all of the monohydroxy derivatives of the simple hydrocarbons, meso-hydroxy-anthracene is the only one which exists largely in the keto form; but when it is recalled that meso-anthraquinone is far more stable than any of the other simple quinones, an adequate account of the stability of anthrone suggests itself: in each case the two benzene nuclei stabilize a quinonoid system.

There is one statement in the book which, though it involves a minor point, cannot be allowed to go unchallenged. It is to the effect that anthraquinone is no true quinone but a diketone. This frequently repeated view probably originated with Willstätter at the time of his brilliant discovery of the quinones of particularly high oxidation potential, and it is easy to see how he came to regard anthraquinone as, to use his conversational word, "trage." He might well have said "sehr trage," but the fallacy is that the adjective used was "zu." The facts are that anthraquinone is a diketone, if a rather inactive one; it is an inactive quinone in the sense that its reduction potential of 0.155 v. is quite low in comparison to the figure of 0.784 v. for a-benzoquinone, though it shares with this compound the distinctive property of undergoing reversible reduction with great rapidity.

L. F. FIESER

The Journal of the
American Chemical Society

VOL. 51 JUNE, 1929 No. 6

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DEPARTMENT, HOLY CROSS COLLEGE NO. 1]

THE VAPOR PRESSURE OF ISOPROPYL ACETATE[1]

BY CECIL J. HAGGERTY AND JOSEPH F. WEILER

RECEIVED JUNE 15, 1928 PUBLISHED JUNE 5, 1929

Introduction

While conducting some experiments recently on the physical properties of binary mixtures of ethyl, n-propyl and isopropyl acetates with acetic acid,[2] in order to make certain calculations with these mixtures it was necessary to know the vapor pressures of the esters. In searching through the literature we were able to find such data on the ethyl and n-propyl acetates,[3] but were unable to discover any vapor pressure work on the isopropyl acetate. In the absence of such data the following investigation was undertaken.

Experimental

The apparatus employed in this work was essentially the same as that recommended by Smith and Menzies,[4] mercury serving as the confining liquid in the U-tube. The thermostat was a glass vessel of about six liters' capacity, provided with a propeller type stirrer and a nichrome wire heating element which was so connected through a lamp bank that the current could be varied at will, and in addition, a small fraction of current operated through a thermoregulator and relay, maintaining the temperature to within ±0.01°. Small Anschütz thermometers were employed along with a Beckmann, which served to denote the variation of temperature of the water-bath. The small thermometers were calibrated against a Bureau of Standards thermometer at the temperatures employed in this work. The manometer was of the ordinary type used in vapor pressure measurements. With the usual precautions it was accu-

---

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

[2] Work to be published later.

[3] Young and Thomas, *J. Chem. Soc.*, 63,1191 (1893).

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

rate to within 0.2 mm. The bulblet and U-tube part of the apparatus were baked at 150° for twenty-four hours in order to remove as much adsorbed water as possible. It was then cooled in a desiccator over sulfuric acid and used immediately when cool.

Preparation of Materials.—*Iso*propyl acetate from the Eastman Kodak Company served as a starting point. This was treated with a solution of potassium carbonate (50 g. in 100 cc.) in order to remove any acid which might be present, and then with a strong solution of calcium chloride (100 g. in 100 cc.) to remove any alcohol. It was allowed to stand over anhydrous calcium chloride overnight and then carefully distilled. Only that fraction which boiled within 0.1° was taken. It is very difficult to purify an ester beyond this point, so this fraction served as a stock solution and the samples employed in the isoteniscope were freshly distilled from it each time. We did not attempt to obtain the boiling point of this fraction accurately for we expected to obtain the true boiling point from the vapor pressure data. The mercury used in the manometer was distilled several times according to the method of Hulett.[5]

Discussion of Error.—At the lower temperatures the main error is due to the variation in reading the manometer. This amounts to about 0.2 mm. At temperatures above 60° the error due to temperature variation should become noticeable and gradually increase up to the maximum temperature employed in this work. The maximum absolute deviation was 0.5 mm. This indicates that providing sufficient readings are made on the manometer the error due to temperature variation may be maintained within the error due to reading the manometer. In order to make sure that these errors were not larger than we anticipated, we ran a determination of the vapor pressure of water and compared the results with those of Smith and Menzies.[6] These results deviated at most by an absolute error of 0.3 mm. The average deviation from the mean of values at 5° intervals from 50 to 80° was 0.2 mm. This shows that our values on the vapor pressure of isopropyl acetate are probably correct to within 0.2 mm. The largest percentage error obtains at the lower temperatures, where it may amount to as much as 1.5%. This percentage error falls off gradually as the temperature is raised.

Method of Procedure.—After the bulblet and U-tube were removed from the desiccator, the bulb was charged with 5–6 cc. of isopropyl acetate and the mercury placed in position in the limb of the U-tube. This part of the apparatus was connected to the manometer and vacuum pump and the whole system evacuated with continuous pumping for about an hour, reducing the volume of isopropyl acetate to about 1–1.5 cc. The mercury was then tipped into position in the U-tube with the pump

---

[5] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

[6] Ref. 4, p. 1430.

still running. The system was disconnected from the pump and the usual procedure followed for determining vapor pressure.

Experimental Data

The vapor pressure measurements on isopropyl acetate are given in Table I. The values in the second column are the average of several readings at the indicated temperatures, while those in Col. 3 are on a different sample and with a different U-tube and bulblet. The fourth column gives the average of the values in 2 and 3, and the last column the calculated values. The experimental readings at each temperature were all taken within a fifteen-minute interval along with the barometric pressure. All pressures are corrected to 0°.

TABLE I

VAPOR PRESSURES OF *ISOPROPYL* ACETATE

Temp., °C.	Vapor press., I	Obs., mm., II	Av. mm.	Calcd. mm.	Temp., °C.	Vapor press., I	Obs., mm., II	Av. mm.	Calcd. mm.
0.00	15.8	15.6	15.7	15.7	50.20	189.4	189.4	189.4	188.8
5.00	21.3	20.9	21.1	21.0	55.20	234.2	233.9	234.1	232.0
10.00	27.9	27.8	27.9	27.8	60.20	284.4	284.2	284.3	281.7
15.00	36.5	36.3	36.4	36.4	65.20	344.1	344.1	344.1	340.3
20.00	47.2	47.0	47.1	47.2	70.20	413.6	413.7	413.7	409.6
25.00	60.8	60.5	60.7	60.6	75.20	493.8	494.0	493.9	490.0
30.00	77.3	77.2	77.3	77.0	80.20	585.4	585.8	585.6	582.5
35.05	98.0	97.7	97.9	97.9	85.20	689.8	690.0	689.9	689.1
40.10	122.9	122.7	122.8	122.6	90.20	810.6	810.9	810.8	811.0
45.15	152.6	152.8	152.7	152.7					

Discussion of Results.—By substitution of the proper constants in the empirical equation of Kirchhoff[7]

$$\log_{10} P = A + B \log_{10} T + C/T$$

we obtained the following equation

$$\log_{10} P = 14.2517 - 2.0972 \log_{10} T - 2170.1/T$$

The values in Col. 5 of Table I were obtained from this equation by substituting the proper temperatures and solving for the vapor pressure. It will be seen that the calculated values agree fairly well with the observed, the maximum percentage error occurring at 65.20°, where it is a little over 1%. This equation may also be used to calculate the boiling point, which is found to be 88.2°.

We have also employed this equation along with the expression $d \ln P/dT = L/RT^2$ in order to determine the molal heat of vaporization at the boiling point. The value so obtained was corrected by deducting 4% according to Parks and Barton,[8] giving a final value of 7900 cal. per mole. This quantity substituted in the Trouton equation gives a molal

---

[7] Kirchhoff, Pogg. ***Ann.,*** 103, 185 (1858).

[8] Parks and Barton, THIS JOURNAL, **50,** 2G (1928).

entropy of vaporization of 21.8 cal. per degree, indicating that *iso*propyl acetate is a normal liquid.

Following Hildebrand,[9] we have also calculated the molal entropy of vaporization at that temperature (35.0° in the case of isopropyl acetate) at which the concentration of the vapor is 0.00507 mole per liter and obtained a value of 27.6 cal. per degree. As 27.4 cal. per degree is the mean value obtained by Hildebrand for normal liquids, this value also indicates that *iso*propyl acetate is a normal liquid.

Summary

Vapor pressure measurements have been made on *iso*propyl acetate from 0 to 90°, inclusive.

An equation has been obtained for the vapor pressure curve from which the boiling point has been determined.

From this equation the molal heat of vaporization has been determined.

The molal entropy of vaporization has been determined at the boiling point and also at that temperature at which the vapor concentration is 0.00507 mole per liter.

These molal entropies indicate that *iso*propyl acetate is a normal liquid.

HOLY CROSS COLLEGE
WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

EQUILIBRIUM BETWEEN THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM IN AQUEOUS SOLUTION AT 25°

BY ARTHUR E. HILL AND STERLING B. SMITH[1]

RECEIVED DECEMBER 3, 1928 PUBLISHED JUNE 5, 1929

A phase-rule study of the reactions between the carbonates and bicarbonates of sodium and potassium does not appear to have been published heretofore. Such a study may be regarded as including the more important part of the possible reactions of the two bases with carbonic acid, between the limits in which the carbonic acid varies from an amount just sufficient to form normal carbonates with all the base present and an amount sufficient to form bicarbonates with all the base present. For such a four-component study, four three-component studies are a preliminary essential; these are listed below. Three of them have been studied with more or less completeness at a number of times and places, and more recently at this

---

[9] Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, New York, 1924, p. 94.

[1] The material of this paper was presented by Sterling B. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1927.

Laboratory with a special view toward their use in the four-component study here reported; the fourth has been studied elsewhere, the results not yet being published.

Na_2CO_3–K_2CO_3–H_2O[2]	K_2CO_3–$KHCO_3$–H_2O[4]
Na_2CO_3–$NaHCO_3$–H_2O[3]	$KHCO_3$–$NaHCO_3$–H_2O[5]

Data from these studies, recalculated so as to be of use in the four-component study, will be introduced later.

Experimental Methods.—The four salts used were Kahlbaum's preparations "zur Analyse." These were found by analysis, after drying, to be pure up to the limit of our most careful standardization, with the exception of the sodium bicarbonate, which showed decomposition into carbonate in amount varying from 0.5 to 3% in various samples. Since sodium carbonate is one of the components of the systems studied, it was necessary merely to correct the weights taken in some cases; in others the correction is wholly unnecessary.

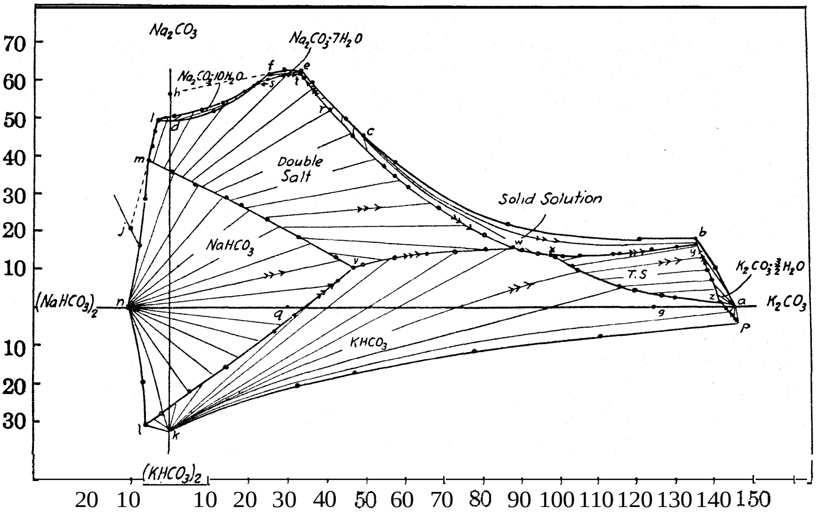


Fig. 1.—K_2CO_3–$NaHCO_3$–Na_2CO_3–$KHCO_3$–H_2O at 25".

In carrying out the solubility experiments, which were intended to give us the lines for saturation with respect to two solid phases later shown in Fig. 1, solutions were prepared corresponding to the isothermally invariant points in the three-component systems (Points 1, m, i, etc., in Fig. 1) or in the four-component system (Points v, w, etc.), with a small excess of the two solid phases present. To each of these was added a small amount of the necessary fourth component, the whole complex being contained in a 50-cc. glass-stoppered Pyrex test-tube. The solubility tubes were then rotated,

---

[2] (a) Kremann and Zitek, *Monatsh.*, **30**, 323 (1909); (b) Osaka, *Mem. Coll. Sci. Eng., Kyoto*, **3**, 51 (1911); (c) Blasdale, THIS JOURNAL, **45**, 2935 (1923); (d) Hill and Miller, *ibid.*, **49**, 669 (1927).

[3] McCoy and Test, *ibid.*, **33**, 473 (1911); (b) Freeth, *Phil. Trans. Roy. Soc.*, *223*, **35** (1922); (c) Hill and Bacon, THIS JOURNAL, **49**, 2487 (1927).

[4] Hill and Hill, *ibid.*, **49**, 967 (1927).

[5] N. E. Oglesby, University of Virginia (unpublished).

with suitable protection against entrance of water, in a thermostat at 25 ± 0.1°; sixteen hours sufficed for the attainment of equilibrium in the majority of cases, but from thirty-six to forty-eight hours were required where one of the phases is a solid solution. For the analysis of the saturated solutions, three samples were withdrawn by pipet in each instance, using a small filter of linen in cases where the liquid did not settle clear, and their weights ascertained. One sample was titrated for total alkali, using hydrochloric acid with methyl orange as indicator; by the use of a color blank for matching end-points, of a constant volume in the titration, and of sodium carbonate as the ultimate standard for the hydrochloric acid, errors in this titration were reduced to a minimum. The second sample was weighed into a platinum dish and evaporated under reduced pressure of about $^1/_6$ atmosphere in a vacuum oven at 80°; after apparent completion of the evaporation, the sample was heated to incipient fusion over a Bunsen burner and brought to a constant weight; the residue gives the total carbonates of the two metals obtained from the solution of carbonates and bicarbonates. The third sample was analyzed for its carbon dioxide content by acidification with sulfuric acid in a suitable train, the gas finally being absorbed by soda lime in a Morgan bottle. From these three operations the complete composition of the solution can be calculated, to be expressed in terms of whatever four components may be most convenient. It is estimated that the errors in the individual analyses are not greater than 0.1%, but the method of indirect calculation multiplies these errors to what may be as great as 1%; the smoothness of the curves, however, indicates that the total errors are less than this amount. Densities of the solutions were known from the weights of the pipetted samples, usually 5 or 10 cc. in volume.

The analysis of a series of solutions by the above method gives a saturation curve for solutions saturated with two solid phases, such as the line m–v in Fig. 1. The terminus of such a curve, detected experimentally by a break in the course of the curve, represents an isothermally invariant point, at which a third solid phase has appeared. Such points were determined from the analysis of two or more solutions obtained by following the curves leading to that point. In all such cases except the Points x, y and z, where one of the solid phases cannot be prepared pure, the invariant composition was checked further by preparing a solution of the composition found, adding the three solid phases believed to be in equilibrium with the solution and rotating the system in the thermostat; if the analysis of the solution was found unchanged after forty-eight hours' rotation of the sample, the point was considered definitely fixed.

Experimental Results

In Table I are given the data for the four three-component systems, recalculated from the original papers so as to show composition in terms of moles of the components per 1000 moles of water. These data appear in part in Fig. 1 upon the boundary lines of the drawing. The abbreviations used to indicate the more complex solid phases are indicated at the head of the table. In accordance with custom, the two bicarbonates are assigned a double molecular weight.

The figures for the fourth of the systems ($NaHCO_3$–$KHCO_3$–H_2O) in Table I have been newly determined here and are in fair agreement with those reported to us privately by Mr. Oglesby.[5]

In Table II are given the data found for the four-component system. The three components necessary (with water) to define the composition are arbitrarily chosen so as to be of greatest convenience for the part of the complete diagram represented. An additional abbreviation for a new tetragene salt, described later in the paper, is included in the table.

TABLE I

THE FOUR THREE-COMPONENT SYSTEMS AT 25°

D.S. = Double salt, Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$; S.S. = Solid solution, $(K_2.Na_2)CO_3 \cdot 6H_2O$

System Na_2CO_3–K_2CO_3–H_2O (Ref. 2d)

Point in Fig. 1	Moles of Na_2CO_3	Moles of K_2CO_3	Solid phases
a	0.0	145.8	$K_2CO_3 \cdot 3/2H_2O$
	10.2	141.0	$K_2CO_3 \cdot 3/2H_2O$
b	18.3	136.0	$K_2CO_3 \cdot 3/2H_2O$ + S.S.
	18.4	121.6	S.S.
	20.1	95.6	S.S.
	22.0	86.8	S.S.
	33.5	65.3	S.S.
	38.6	57.7	S.S.
	49.8	44.8	S.S.
	59.5	36.3	S.S.
e	62.7	33.5	S.S. + $Na_2CO_3 \cdot 7H_2O$
	62.9	29.3	$Na_2CO_3 \cdot 7H_2O$
f	61.7	25.4	$Na_2CO_3 \cdot 7H_2O$ + $Na_2CO_3 \cdot 10H_2O$
	58.7	21.2	$Na_2CO_3 \cdot 10H_2O$
	52.0	11.1	$Na_2CO_3 \cdot 10H_2O$
d	49.2	0.0	$Na_2CO_3 \cdot 10H_2O$

System Na_2CO_3–$NaHCO_3$–H_2O (Ref. 3c)

Point in Fig. 1	Moles of Na_2CO_3	Moles of $(NaHCO_3)_2$	Solid phases
n	0.0	10.99	$NaHCO_3$
	3.98	9.82	$NaHCO_3$
	16.07	7.66	$NaHCO_3$
	22.11	7.05	$NaHCO_3$
	28.39	6.45	$NaHCO_3$
m	38.79	5.49	$NaHCO_3$ + D.S.
	40.78	4.92	D.S.
	42.34	4.40	D.S.
	46.37	3.49	D.S.
	49.52	2.97	D.S. + $Na_2CO_3 \cdot 10H_2O$
	49.37	2.24	$Na_2CO_3 \cdot 10H_2O$
	49.36	1.52	$Na_2CO_3 \cdot 10H_2O$
	49.04	1.20	$Na_2CO_2 \cdot 10H_2O$
d	49.20	0.0	$Na_2CO_3 \cdot 10H_2O$

System K_2CO_3–$KHCO_2$–H_2O (Ref. 4)

Point in Fig. 1	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
a	145.8	0.0	$K_2CO_3 \cdot 3/2H_2O$
P	146.8	4.32	$K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$
	110.8	7.70	$KHCO_3$
	78.1	11.41	$KHCO_3$
	47.3	17.02	$KHCO_3$
	32.8	20.57	$KHCO_3$
k	0.0	32.53	$KHCO_3$

TABLE I (Concluded)

System $NaHCO_3$–$KHCO_3$–H_2O

Point in Fig. 1	Moles of $(NaHCO_3)_2$	Moles of $(KHCO_3)_2$	Solid phases
k	0.0	32.53	$KHCO_3$
1	6.17	31.05	$KHCO_3$ + $NaHCO_3$
	7.60	19.4	$NaHCO_3$
n	10.99	0.0	$NaHCO_3$

TABLE II

EQUILIBRIUM $K_2CO_3 + 2NaHCO_3 \rightleftharpoons 2KHCO_3 + Na_2CO_3$ IN WATER AT 25°

T.S. = Tetragene salt, $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

Point in Fig. 1	Density	Moles of Na_2CO_3	Moles of $(NaHCO_3)$	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
m	1.216	38.79	5.49	...	...	$NaHCO_3$ + D.S.
	1.236	35.89	6.21	6.82	...	$NaHCO_3$ + D.S.
	1.256	32.38	7.25	13.66	. .	$NaHCO_3$ + D.S.
	1.279	28.95	8.26	22.62	. .	$NaHCO_3$ + D.S.
	1.297	26.91	9.06	27.21	...	$NaHCO_3$ + D.S.
	1.314	23.39	10.30	35.23	. .	$NaHCO_3$ + D.S.
	1.345	18.52	12.07	44.86	.	$NaHCO_3$ + D.S.
	1.375	13.50	14.08	56.61	...	$NaHCO_3$ + D.S.
v	1.390	10.70	15.40	62.18	...	$NaHCO_3$ + D.S. + $KHCO_3$
1	1.196	...	6.17	...	31.05	$NaHCO_3$ + $KHCO_3$
	1.208	4.62	2.05	...	32.55	$NaHCO_3$ + $KHCO_3$
	1.232	8.85	...	5.07	30.95	$NaHCO_3$ + $KHCO_3$
	1.264	11.23	...	14.52	27.07	$NaHCO_3$ + $KHCO_3$
	1.310	15.80	...	26.93	22.21	$NaHCO_3$ + $KHCO_3$
	1.331	18.34	...	31.95	20.23	$NaHCO_3$ + $KHCO_3$
	1.378	25.88	...	42.98	16.64	$NaHCO_3$ + $KHCO_3$
v	1.390	10.70	15.40	62.18	...	$NaHCO_3$ + $KHCO_3$ + D.S.
p	1.558	...	...	146.8	4.32	$K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$
	1.56	4.22	...	143.8	4.73	K_2CO_3 $3/2H_2O$ + $KHCO_3$
z	1.559	1.35	4.71	146.9	...	$K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$ + T.S.
i	...	49.52	2.97	...	. .	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.262	50.46	2.59	3.48	. .	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.294	52.08	2.11	10.22	. .	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.310	54.04	1.65	15.03	. .	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.334	57.27	1.05	20.02	.	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.347	58.56	1.00	22.35	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
s	1.358	59.20	0.78	23.40	.	D.S. + $Na_2CO_3 \cdot 10H_2O$ + $Na_2CO_3 \cdot 7H_2O$
s	1.358	59.20	0.78	23.40	. .	D.S. + $Na_2CO_3 \cdot 10H_2O$ + $Na_2CO_3 \cdot 7H_2O$
	1.365	60.40	0.82	25.69	. .	D.S. + $Na_2CO_3 \cdot 7H_2O$
	1.381	61.37	0.51	29.59	...	D.S. + $Na_2CO_3 \cdot 7H_2O$
t	1.396	61.77	0.37	34.01	...	D.S. + $Na_2CO_3 \cdot 7H_2O$ + S.S.
t	1.396	61.77	0.37	34.01	. .	D.S. + $Na_2CO_3 \cdot 7H_2O$ + S.S.
	1.403	60.95	0.52	34.74	. .	D.S. + S.S.
	1.396	56.53	0.60	38.32	. .	D.S. + S.S.
	1.396	52.56	0.84	41.70	. .	D.S. + S.S.
	1.399	45.51	1.36	48.16	.	D.S. + S.S.
	1.410	37.58	2.36	57.15		D.S. + S.S.
	1.414	34.86	2.92	60.11	...	D.S. + S.S.

TABLE II (*Concluded*)

Point in Fig. 1	Density	Moles of Na_2CO_3	Moles of $(NaHCO_3)$	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
	1.422	32.15	3.38	64.21	. .	D.S. + S.S.
	1.434	26.04	4.84	73.65		D.S. + S.S.
	1.458	19.27	7.03	87.65		D.S. + S.S.
w	1.481	15.90	8.23	96.45		D.S. + S.S. + $KHCO_3$
w	1.481	15.90	8.23	96.45		D.S. + S.S. + $KHCO_3$
	1.484	15.10	8.17	98.78		S.S. + $KHCO_3$
	1.490	14.13	7.87	102.5		S.S. + $KHCO_3$
x	1.496	13.73	7.46	105.8		S.S. + $KHCO_3$ + T.S.
v	1.390	10.70	15.40	62.18		$NaHCO_3$ + D.S. + $KHCO_3$
	1.391	11.56	14.71	63.92	...	D.S. + $KHCO_3$
	1.413	13.24	12.79	70.18	...	D.S. + $KHCO_3$
	1.433	14.11	11.30	76.92	...	D.S. + $KHCO_3$
	1.446	14.80	10.15	83.35		D.S. + $KHCO_3$
	1.462	15.17	9.19	90.18		D.S. + $KHCO_3$
w	1.481	15.90	8.23	96.45		D.S. + $KHCO_3$ + S.S.
x	1.496	13.73	7.46	105.8		S.S. + $KHCO_3$ + T.S.
	1.497	13.57	6.85	107.9		S.S. + T.S.
	1.507	13.89	5.83	111.7		S.S. + T.S.
	1.521	14.03	4.25	118.8	...	S.S. + T.S.
	1.524	14.42	3.94	120.2	...	S.S. + T.S.
	1.542	15.43	2.71	127.3	...	S.S. + T.S.
	1.550	15.96	2.04	133.1	...	S.S. + T.S.
y	1.563	16.66	1.68	137.7		S.S. + T.S. + $K_2CO_3.3/2H_2O$
x	1.496	13.73	7.46	105.8		$KHCO_3$ + S.S. + T.S.
	1.501	13.30	7.38	106.8		$KHCO_3$ + T.S.
	1.502	10.92	7.23	111.0		$KHCO_3$ + T.S.
	1.504	9.98	7.36	112.4		$KHCO_3$ + T.S.
	1.517	5.62	6.87	122.9	...	$KHCO_3$ + T.S.
	1.531	4.63	6.61	126.8	...	$KHCO_3$ + T.S.
	1.536	3.42	6.12	133.0	...	$KHCO_3$ + T.S.
	1.543	2.49	6.35	136.8	...	$KHCO_3$ + T.S.
z	1.559	1.35	4.71	146.9		$K_2CO_3.3/2H_2O$ + $KHCO_3$ + T.S.
y	1.563	16.66	1.68	137.7		S.S. + T.S. + $K_2CO_3.3/2H_2O$
	1.560	11.73	2.30	140.8		T.S. + $K_2CO_3 \cdot 3/2H_2O$
	1.558	10.04	2.70	141.7		T.S. + $K_2CO_3 \cdot 3/2H_2O$
	1.560	7.38	3.22	143.3		T.S. + $K_2CO_3 \cdot 3/2H_2O$
z	1.559	1.35	4.71	146.9		T.S. + $K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$

Discussion of the 25° Isotherm

The preceding table gives the eleven curves for solubility equilibria with two and with three solid phases. In addition there are the three curves b–y, e–t and f–s which are so short that only their end-points could be determined. All fourteen are shown in Fig. 1, together with the fields representing saturation with respect to a single solid phase; the results are plotted according to the conventional method of Löwenherz.[6] The points

---

[6] Löwenherz, *Z. physik. Chem.*, 13, 459 (1894).

s, t, v, w, x, y and z represent the seven isothermally invariant points, at which the solution is in equilibrium with three solid phases.

Of the eight fields of saturation with a single salt, seven represent salts found in the four three-component systems. Of these the field bounded by the lines b–e–t–w–x–y–b represents the phase recently shown[zd] to be a solid solution, of the formula $(K_2,Na_2)CO_3 \cdot 6H_2O$, and previously thought to be a definite compound of the formula $KNaCO_3 \cdot 6H_2O$. The field for the decahydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, is bounded by the lines i–d–f–s–i; its apparent extension beyond the boundary line for the three-component system (d–f) is, of course, wholly a matter of the Lowenherz method of representation. The eighth field, x–y–z, represents a new tetragene salt, $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which does not occur in any of the three-component systems at this temperature.

The Tetragene Salt.—Upon finding the existence of the field x–y–z, experiments were conducted to determine the composition of the salt which crystallized out within that area. A number of isothermal evaporations of such solutions were carried out, for the purpose of studying the crystallization paths described later. The crystals thus obtained were filtered off, centrifuged at a rate of 1000 r.p.m., which unfortunately was too slow to secure very complete expulsion of the mother liquor, and analyzed in this slightly moist condition. The results of the analysis are given in Table III.

TABLE III

ANALYSIS OF TETRAGENE SALT

Calculated for the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$: K_2CO_3 = 53.52; $NaHCO_3$ = 32.53; H_2O = 13.95%

wt. % K_2CO_3	wt. % $NaHCO_3$	wt. % H_2O	wt. % Na_2CO_3	wt. % K_2CO_3	wt. % $NaHCO_3$	wt. % H_2O	wt. % Na_2CO_3
52.80	31.17	15.17	0.90	54.32	32.05	14.68	−1.05
52.87	31.24	15.24	0.65	55.49	33.29	14.90	−3.68
52.39	28.49	18.48	0.64	55.29	29.86	14.79	0.06
54.17	32.66	14.37	−1.20	53.54	30.19	16.82	−0.55
53.80	32.34	15.05	−1.19	53.63	36.55	14.63	−4.81

In the above table the fourth column is included to represent the actual results as calculated for a possible four-component body. The variations from the composition assumed are not inconsiderable. How far they may be due to occlusion of mother liquor or to precipitation of metastable salts we are not in a position to estimate, but the evidence seems to us convincing that the salt has the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. This would put the compound in the comparatively small class of salts built up of two cations and two anions, to which Meyerhoffer[7] has given the name of "tetragene salts." It is perhaps also worthy of note that the composition of the salt is that of the well-known double salt Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), with

---

[7] Meyerhoffer, *Z. anorg. Chem.*, 34, 147 (1902).

the substitution of a molecule of potassium carbonate for one of sodium carbonate.

In order to verify the formula by a different method, 200 g. of solution was prepared of a composition known to fall in the desired area. **A** small amount of the solid was added and the mixture rotated in the thermostat at 25° for 120 hours. At the end of that time the solid phase had not disappeared, indicating that equilibrium existed between the solid and liquid phases. The crystals were then allowed to settle and the liquid was analyzed. The composition of this solution is represented by a point within the field x–y–z and is as follows: $Na_2CO_3 = 3.26$; $NaHCO_3 = 1.87$; $K_2CO_3 = 46.62$; $H_2O = 48.25$. To the above equilibrium mixture was added 13.82 g. of K_2CO_3, 8.4 g. of $NaHCO_3$ and 3.6 g. of H_2O, corresponding to the composition of the alleged salt, $K_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$. The mixture was again rotated in the thermostat for forty-eight hours and the solution analyzed. This solution gave the following analysis: $Na_2CO_3 = 3.30$; $NaHCO_3 = 1.85$; $K_2CO_3 = 46.71$; $H_2O = 48.14$. Since the analyses of these two solutions agree within a small experimental error, the composition of the liquid phase may be regarded as unchanged and the solid phase is shown to have the composition $K_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$.[8]

Crystallization Paths.—In Fig. 1 the lines drawn within the fields represent crystallization paths of solutions undergoing isothermal evaporation. Except for the field x–y–z, for which experimental data will be given later, these lines have been drawn according to the conventional *a priori* reasoning, assuming that solid phases are withdrawn as formed; they therefore can represent only in a qualitative way the course of such evaporations. In the case of the four salts $Na_2CO_3{\cdot}10H_2O$, $K_2CO_3{\cdot}3/2H_2O$, $KHCO_3$ and $NaHCO_3$, the solubilities in water are represented by the four points d, a, k and n, falling on the respective axes; the crystallization paths for these salts are therefore drawn as radiating from these points. The heptahydrate, $Na_2CO_3{\cdot}7H_2O$, is not stable in water at this temperature, but its solubility may be estimated by extrapolation of its solubility curve e–f to the point h, from which center its crystallization paths radiate. The point for the crystallization paths of the double salt Trona also has to be found by extrapolation of its solubility curve i–m to a point on a line representing its molecular composition, namely, the point j. For the solid

---

[8] Since this paper was written there has appeared Teeple's "The Industrial Development of Searles Lake Brines," Chemical Catalog Company, New York, 1929, in which appears (p. 132) a study of this four component system at 35°, carried out by Harald de Ropp. The field which we assign at 25° to the tetragene salt $K_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$ is assigned by them at 35° to a potassium sesquicarbonate, $K_2CO_3{\cdot}2KHCO_3{\cdot}3H_2O$. Without raising any question as to the correctness of de Ropp's findings at 35°, we have not found the potassium sesquicarbonate at 25°, and are sure that the salt found by us is a sodium–potassium salt in the atomic ratio of 1:2, as we have reaffirmed by repeated analyses.

solution $(Na_2,K_2)CO_3 \cdot 6H_2O$ we cannot speak of a definite solubility in water, for the solid phase has a varying composition; the crystallization paths therefore will radiate not from a single point but from a series of points. By drawing lines from the origin in the coordinate system so as to represent the atomic ratios of sodium to potassium in the extreme compositions found for the solid solution, it was found that the two lines intersect the solubility curve e–b close to the point e and at c; the crystallization paths will therefore radiate from a series of points between e and *c*. These lines are drawn in this area with a considerable curvature, to correspond with the curvature of the line e–b; elsewhere in the diagram they are drawn arbitrarily as straight lines, or lines with but a slight curvature.

The crystallization paths for the remaining phase, the tetragene salt, were investigated experimentally; a *priori* it could only be deduced that the center of the radiating lines would fall somewhere between the point representing the composition of the salt and the origin of the coordinate system. For the experiments large quantities of solutions were prepared of compositions lying near to the line x–z. Each of these was inoculated with a

TABLE IV

CRYSTALLIZATION PATHS IN THE AREA X–Y–Z–(TETRAGENE SALT)

		Initial solution				Final solution	
		Wt. %	Moles per 1000 of H_2O	Wt. %	Moles per 1000 of H_2O	Wt. %	Moles per 1000 of H_2O
Curve 1	Na_2CO_3	3.63	12.43	3.70	12 80	4.11	14.43
	$(NaHCO_3)_2$	2.62	5.66	2.08	4.54	1.55	3.43
	K_2CO_3	44.11	115 8	45.11	119.7	45.95	123.8
	H_2O	49.64	....	49.11	....	48.39	....
Curve 2	Na_2CO_3	2.97	10.15			3.42	12.61
	$(NaHCO_3)_2$	2.82	6.08			1.15	2.68
	K_2CO_3	44.50	116.7			49.33	139.5
	H_2O	49.71	....			46.10	....
Curve 3	Na_2CO_3	2.72	9.35			3.10	10.89
	$(NaHCO_3)_2$	2.70	5.85			1.86	4.12
	K_2CO_3	45.13	119.0			46.67	125 8
	H_2O	49.45	....			48.37	....
Curve 4	Na_2CO_3	2.43	8.31			3.23	11.85
	$(NaHCO_3)_2$	3.27	7 05			0.88	2.04
	K_2CO_3	44.57	1168			49.58	139.6
	H_2O	49.73	....			46.31	....
Curve 5	Na_2CO_3	2.28	7.78			3.25	11.86
	$(NaHCO_3)_2$	3.49	7.51			1.17	2.69
	K_2CO_3	44.43	116.3			49.03	137.3
	H_2O	49.80	....			46.55	....
Curve 6	Na_2CO_3	1.95	6.72			2.67	9.84
	$(NaHCO_3)_2$	3.33	7.25			1.20	2.79
	K_2CO_3	45.44	120.2			50.01	141.4
	H_2O	49.28	....			46.12	....

small amount of crystalline tetragene salt and rotated in the thermostat for forty-eight hours to secure equilibrium; after being allowed to settle, the clear liquid was analyzed. The remaining material was then placed in an evaporating dish in a desiccator over concentrated sulfuric acid and maintained in an air thermostat at 25°. The solutions were stirred from day to day and were weighed at frequent intervals to follow the rate of evaporation. In the course of three weeks about 20 g. of water was lost by each and a quantity of solid phase obtained sufficient for analysis. The mixtures were then again rotated in the thermostat at 25° for forty-eight to seventy-two hours to secure equilibrium and the solid phase was filtered off; the analysis of ten such samples has been given previously in Table III. The liquid phases were then analyzed. The results of the initial and final analysis for six such experiments are given in Table IV and shown in Fig. 2 by the points within the area x–y–z; connecting these by straight lines (as the simplest assumption) we obtain a series of crystallization paths for the tetragene salt.

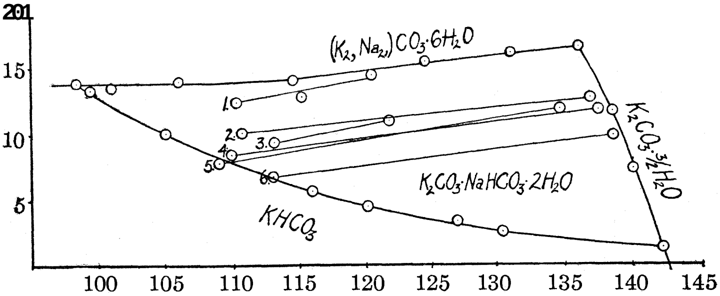


Fig. 2.—Crystallization paths for the tetragene salt, $K_2CO_3 \cdot NaHCO_3$-$2H_2O$ at 25°.

If the crystallization paths thus found and shown in Fig. 2 be extrapolated, they will fall close to the point in Fig. 1 represented by q.

With the crystallization paths for the eight single solids determined, the direction of the crystallization paths along the lines for two-solid equilibrium follows. Of these fourteen curves for isothermally univariant equilibrium, only three are not crystallization paths; these are the Curves m–v, s–f and x–z. At each of these curves resorption of the solid phase present takes place, with separation of a new solid phase; the changes represented are, respectively

$$NaHCO_3 \longrightarrow NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O \text{ (Trona)}$$
$$Na_2CO_3 \cdot 10H_2O \longrightarrow Na_2CO_3 \cdot 7H_2O$$
$$KHCO_3 \longrightarrow K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O \text{ (Tetragene salt)}$$

Isothermally Invariant Points.—The fourteen isothermally univariant curves meet at seven points, which represent saturation with respect to three solid phases in each case and are therefore isothermally invariant.

Inspection of the curves meeting at these points shows, however, that in only two of the seven cases are the points the termini of three crystallization lines; these are the points t and y, which are therefore crystallization end-points or drying-up points. Solutions of any possible composition will, therefore, under isothermal evaporation, go to dryness at one or another of these two points, with the precipitation of the three salts indicated, namely at t, $Na_2CO_3 \cdot 7H_2O$, Trona and the solid solution, and at y, $K_2CO_3 \cdot 3/2H_2O$, solid solution and the tetragene salt. The other five points are not points of congruent saturation.

There is also in the system a single point of congruent saturation with respect to two solid phases, namely, Trona and the solid solution; the point has been set arbitrarily, without experimental confirmation, at r. This point represents the position for dividing the possible solutions of the system into two classes: those falling to the right of the crystallization paths leading to r will dry up at the point y, and those to the left will dry up at t, the division depending chiefly upon the total amounts of sodium salts and of potassium salts which are present.

Summary

1. The 25° isotherm has been studied for the quaternary system made up from sodium carbonate, potassium bicarbonate and water, and the results have been plotted according to the method of Löwenherz.

2. The system has been found to contain eight fields of isothermally bivariant equilibrium, fourteen lines of isothermally univariant equilibrium and seven isothermally invariant points.

3. There is no "stable pair" in this system at this temperature; *i. e.*, neither Na_2CO_3 and $KHCO_3$ nor $NaHCO_3$ and K_2CO_3 can be in equilibrium as solid phases.

4. A new tetragene salt has been found, of the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, not occurring in any of the three-component systems.

5. The crystallization paths for the tetragene salt have been studied experimentally, and the paths for the other salts have been deduced *a priori*.

6. There exist in the system at this temperature two crystallization end-points and one two-solid congruent point.

NEW YORK, N. Y.

[Contribution from the Chemical Laboratory of the University of Michigan]

AN INTERFEROMETRIC INVESTIGATION OF ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS[1]

By F. E. Bartell and C. K. Sloan[2]

Received December 10,1928 Published June 5, 1929

Measurements which have been carried out for the purpose of relating the change in concentration to adsorption have, in practically all cases, been made by means of volumetric or gravimetric methods. Surprisingly few of the investigators have made use of the measurement of refractive index. In the present investigation a Rayleigh interferometer (made by Hilger) was used. Standard methods were employed for the purification of liquids.

For one who is attempting to master the technique of the interferometric method as applied to liquids the papers of Adams,[3] Cohen and Bruins,[4] and Barth and Schaum[6] are of great value. Mitchell[6] and Macy[7] have recently described the use of the instrument for the measurement of the concentration of very dilute aqueous solutions. Others have found interferometry useful in adsorption problems. Odkn and Anderson[8] used the interferometer to study the adsorption of the cations of alkali and alkaline earth materials by carbon. In like manner, Ruff[9] determined the amount of phenol adsorbed from solution by a number of commercial carbons. Oliphant and Burdon[10] used the interferometer to measure adsorption of gas on mercury droplets. Others who have made use of interferometry in the study of adsorption from solution include Marc,[11] Wolff,[12] Arendt[13] (who studied the velocity of adsorption by this method), Berl and Wachendorff,[14] and Patrick and Jones.[15]

Preparation and Properties of Carbon.—Bartell and Miller[16] have

---

[1] The material presented in this paper is from a dissertation submitted by C. K. Sloan to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] DuPont Fellow in Chemistry, 1927–1928.

[3] Adams, This Journal, 37, 481, 1181 (1915).

[4] Cohen and Bruins, *Z. physik. Chem.*, 103, 337 (1923).

[5] Barth and Schaum, *Z. wiss. Phot.*, 24, 145, 158, 166 (1926).

[6] Mitchell, *J.* Chem. *Soc.*, 129, 1333 (1926).

[7] Macy, This Journal, 49, 3070 (1927).

[8] Odén and Anderson, J. *Phys. Chem.*, *25*, 311 (1921).

[9] **Ruff,** *Kolloid-Z.*, 38, 59 (1926).

[10] Oliphant and Burdon, ***Nature,*** 120, 584 (1927).

[11] Marc, *Z. physik. Chem.*, *81*, 641 (1913).

[12] Wolff, *Kolloid-Z.*, 32, 17 (1923).

[13] Arendt, *Kolloid Chem. Beihefte*, *7*, 212 (1915).

[14] Berl and Wachendorff, *Kolloid-Z.*, ***36,*** 36 (1925).

[15] Patrick and Jones, J. *Phys. Chem.*, 29, 1 (1925).

[16] Bartell and Miller, This Journal, 44, 1866 (1922).

emphasized the importance of the use of pure carbon in adsorption experiments. They worked out a method for the activation of charcoal prepared by the carbonization of recrystallized sugar. This method, with but slight modification, was used for the preparation of a pure active carbon. The activity of the carbon was tested according to directions given by Miller.[17] It was found that a quarter of a gram of carbon was capable of removing 54% of the benzoic acid from 100 cc. of a 0.02 N solution during ten minutes of intermittent shaking. Miller states that a fairly active carbon will adsorb 50% of the benzoic acid under these conditions. It is possible to prepare a more active carbon but this involves a greater loss in carbon due to oxidation. Eor the present work it was thought advisable to limit the activation treatment to four hours. A sufficiently active carbon can be obtained during that period without too greatly cutting down the yield. One hundred grams of Merck's saccharose will give about twelve grains of char. Heating this char in nitrogen at 900° reduces the amount to nine grams. The four-hour intermittent activation leaves about five grams of active carbon. After a sufficient quantity is obtained, it should be heated to drive off adsorbed moisture and then kept in a desiccator. It was found that the carbon which had been used for the adsorption of volatile organic liquids can be recovered without changing its adsorptive capacity appreciably.

Modification of Apparatus.—Activated carbon was added to different aqueous solutions of such substances as pyridine, aniline, benzene and a number of acids and alcohols. After a small amount of activated carbon had been added to a saturated solution of benzene in water, the interferometer indicated that all of the benzene had been adsorbed. In each of the other cases a pronounced adsorption of solute occurred. Because of the very slight solubility of many of these substances in water, it was thought desirable to study adsorption from a non-aqueous solvent. The interferometer, however, cannot be used without modification for the analysis of such solutions since organic liquids usually have a higher volatility, a higher temperature coefficient of refractivity and a lower heat capacity than water. Unless certain precautions are taken, these factors result in distortion of the interference band system and uncertainty in the instrument reading. Cohen and Bruins[4] found it necessary to keep their interferometer (Zeiss type) in a water thermostat. A brass plug was made to fill all of the space above the liquid in their interferometer cell in order to prevent evaporation and distillation of liquid against the cover plate of the cell. A few attempts at measuring the concentration of non-aqueous solutions made evident the necessity of considering the precautions given by Cohen and Bruins. The compartments of the cell (Fig. 1) of the Hilger interferometer at first were covered with a plane glass plate. In many cases liquid filled the space between the cell and its cover even though great care was taken in filling the compartments. This liquid slowly evaporated. After the entire instrument had been placed in the large air thermostat used for temperature regulation, loss of liquid due to evaporation was still more pronounced because of the greater circulation of air around the cell. A steel cover was designed to fit over the top of the cell, permitting a mercury seal between the glass of the cell and the cover (Figs. 1 and 2). The under side of the latter carries a groove one-sixteenth of an inch wide extending

---

[17] Miller, *J. Phys. Chem.*, 30, 1162 (1926).

around the top of the glass cell and across the center between the two compartments. This groove is one-quarter of an inch deep and when filled with mercury serves as an effective means of preventing evaporation. A small hole at each end of the top of the cover permits filling the grooves with mercury after the cover is in place on the cell. Liquid is introduced into the compartments through two holes extending through the cover. Mercury seals around each of these holes prevent evaporation at these points.

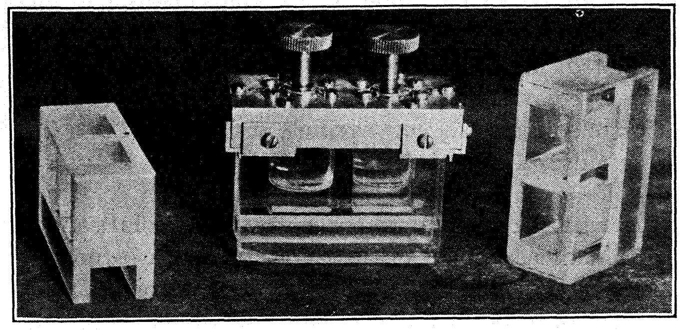


Fig. 1.

Preparation of Solutions and Method of Measurement.—All solutions were made up by weight, the most concentrated being made first and the others obtained by dilution of this with weighed amounts of solvent. The adsorption was carried out in long slender bottles with narrow necks tightly fitted with glass stoppers. The weight of carbon, m, was determined by weighing the flask before and after introduction of about a quarter of a gram of carbon. About 5 cc. of solution was then introduced and the increase in weight, N, determined. The adsorption bottles were then shaken for twenty hours and put in the air thermostat at 25°. The original solutions were also kept at this temperature for a few hours before making concentration determinations. A portion of the liquid was then removed from the carbon and compared with the original solution in the interferometer cell.

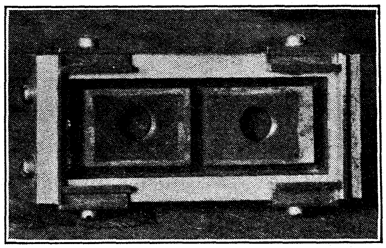


Fig. 2.

The solution of known concentration is always placed in the left-hand compartment of the cell. With this arrangement an interferometer reading greater than the zero reading indicates that the refractive index of the unknown solution is the greater. A calibration is required to determine the difference in concentration corresponding to this reading. This is made by comparing two solutions of known concentration which permits a calculation of the rate of change of concentration with instrument reading (dc/dR). It is highly desirable to compare the solution of unknown concentration with one of nearly the same concentration. If the concentration interval is too great, correction must be made for the change in appearance of the color fringes of the interference system. This phenomenon is fully discussed by Barth and Schaum.[5] A series of calibrations in the range between zero and one per cent. of α-bromonaphthalene in alcohol shows the sensitivity of the method. One division of the interferometer is equivalent to a difference in weight concentration of 0.0000205(dc/dR = 0.0000205). The concentration interval must be equivalent to less than fifty scale divisions; otherwise there may be some difficulty in matching the bands correctly. In many cases adsorption is so great that the equilibrium liquid has to be compared with a solution of known concentration which differs from it less than does the original solution.

Calculation of Data

The Freundlich adsorption equation has been found to apply to the adsorption of solutes when present in low concentration. The degree of adsorption from more concentrated solutions is lower than the equation would indicate. This equation states that the weight of solute removed per gram of adsorbent is proportional to a certain power of the equilibrium concentration of solute. Letting w represent the weight of solute adsorbed by m grams of adsorbent

$$w/m = a'c^n \tag{1}$$

where c represents the equilibrium concentration of solute and a' and n are constants. The measurement of the refractive index before and after adsorption gives directly the change in concentration of the solution rather than the weight of solute removed. For a small change in concentration of solute due to removal by adsorption, the change (Ac) is directly proportional both to the weight of solute removed (w) and to the concentration of solvent $(1 - c)$, whereas it is inversely proportional to the total amount of solution N. We have, therefore, the relationship

$$\Delta c = a''w(1 - c)/N \tag{2}$$

Solving for w and substituting in Equation 1 gives

$$N\Delta c/(1 - c)m = ac^n \tag{3}$$

or

$$N\Delta c/m = ac^n(l - c) \tag{4}$$

If we plot a curve from data obtained with the above equation, using $N\Delta c/m$ as one coördinate and c as the other, we find that the first portion of the curve is similar to the ordinary adsorption isotherm. The second term $(1 - c)$, however, soon becomes prominent and causes the curve to pass through a maximum and then decrease to zero when c becomes unity. In this extreme case there would, of course, be no change in concentration even though a maximum of solute were adsorbed. It is evident that the change in concentration at these higher concentrations must be measured very accurately to determine whether the Freundlich equation is applicable. The measurement of refractive index with the interferometer is sufficiently accurate for this purpose.

The adsorption was first expressed in terms of $N\Delta c/m$. In order to compare the adsorption of different substances on a common basis, it was thought desirable to substitute molar units for weight units. Letting x represent the molar concentration, M_1 the gram molecular weight of solute and M_2 the gram molecular weight of solvent, we have

$$x = \frac{1}{1 + M_1(1 - c)/M_2c}$$

Letting H represent the total number of millimoles in solution and Ax the change in molar fraction due to adsorption, it can be shown that

$$H\Delta x/m = (1000x/M_2c)(Nc/m)$$

Results

Some of the results obtained are given in the following tables.

TABLE I

ADSORPTION OF α-BROMONAPHTHALENE FROM ETHYL ALCOHOL[a]

c_0	c	Δc	$N\Delta c/m$	x	$H\Delta x/m$
0.00400	0.00382	0.000178	0.0611	0.0000395	0.1718
.00600	.0056	.000435	.0885	.0000966	.2502
.00800	.00723	.000763	.1157	.0001696	.3255
.01000	.00863	.001367	.1377	.0003037	.3882

[a] The initial and final concentrations are represented by c_0 and c_1, respectively.

TABLE II

ADSORPTION OF BENZENE PROM ETHYL ALCOHOL

c_0	m	Ac	c	$N\Delta c/m$	x	$H\Delta x/m$
0.01102	0.2174	0.00236	0.00866	0.0405	0.00513	0.621
.02160	.2327	.00389	.01771	.0611	.01050	0.787
.04335	.2202	.00516	.03819	.0862	.02289	1.123
.08621	.2181	.00661	.07960	.1161	.04854	1.537
.1718	.2170	.00848	.1633	.1473	.1033	2.022

TABLE III

ADSORPTION OP ETHYL CARBONATE FROM ETHYL ALCOHOL

c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.00865	0.00042	0.00823	0.010	0.00323	0.084
.01765	.00073	.0170	.015	.00667	.132
.03570	.0014	.0343	.028	.0136	.24
,07178	.0018	.0700	.041	.0286	.360
.1429	.00292	.1400	.061	.0596	.566

Discussion

The foregoing tables and graph indicate that the adsorption by carbon of the three solutes, α-bromonaphthalene, benzene and ethyl carbonate from ethyl alcohol is in accordance with the Freundlich equation ($H\Delta x = ax^n(l - x)$) for the low concentrations investigated. The constants of the equations representing the adsorption of these substances from dilute alcoholic solution are given in the table below, together with the adhesion-tension[18] value of each against carbon.

Solute	a	n	Adhesion tension
a-Bromonaphthalene	12.1	0.42	89.2
Benzene	9.79	.53	81.1
Ethyl carbonate	4.9	.72	65.6"

[a] Unpublished data.

---

[18] Bartell and Osterhof, Z. *physik.* Chem., 130, 715 (1927); *Ind. Eng.* Chem., **19,** 1277 (1927).

The order of adsorption from dilute solutions is the same as that of the adhesion tension of the solutes investigated. The coefficient, a, of the Freundlich equation increases in the same order as the adhesion-tension values, while the exponents are in the inverse order. Each of these variations corresponds to an increase in adsorption with increase in adhesion tension. Adhesion tension (A_{12}) is defined as the difference between the surface tension (S_1) of the solid and the interfacial tension (S_{12}) existing at the solid–liquid boundary.

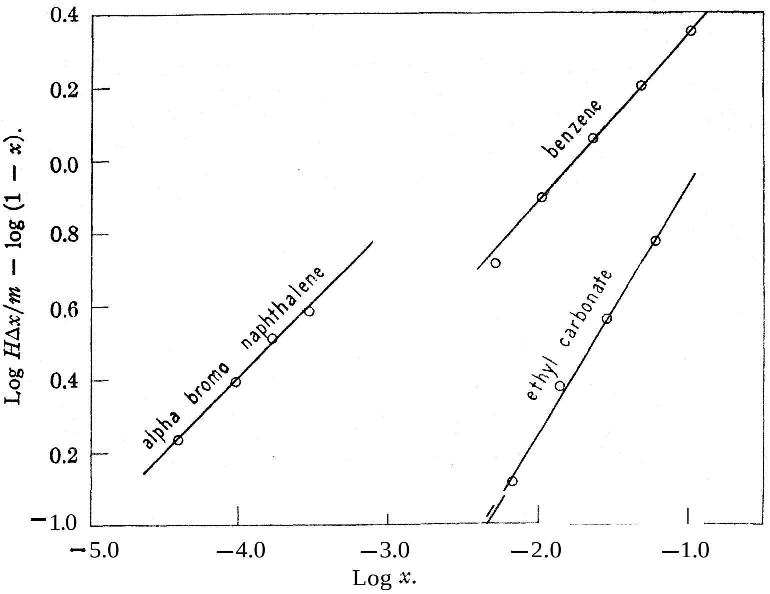


Fig. 3.—Adsorption by carbon from ethyl alcohol.

$$A_{12} = S_1 - S_{12}$$

The adhesion tension, then, is a measure of the decrease in free surface energy which occurs when the solid–liquid interface is substituted for the solid–air interface. It is a measure of the degree to which the solid is wetted by a liquid. The Gibbs principle indicates that greatest adsorption will occur from that system which will produce the greatest lowering of interfacial tension. It may accordingly be reasoned that a liquid which is highly adsorbed by a solid will give a low interfacial tension against that solid. Furthermore, a liquid which with a given solid has a low interfacial tension will in general show a high adhesion tension with it. It is to be expected, then, disregarding solubility effects, that a-bromonaphthalene will be adsorbed to a greater extent from ethyl alcohol than will either benzene or ethyl carbonate because there will be relatively a greater decrease in the free surface energy of the system when a-bromonaphthalene comes in contact with the carbon surface.

Summary

1. The use of the interferometer in measuring the change in concentration due to adsorption from non-aqueous solutions is discussed.

2. Data are given for the adsorption by carbon of α-bromonaphthalene, benzene and ethyl carbonate from dilute solutions in ethyl alcohol.

3. It is pointed out that the adsorption of these solutes by carbon tends to be in the same order as the adhesion-tension values of these same solutes (as pure liquids) against carbon. It is probable that this relationship would obtain in all cases were it not for the influence of other factors such, for example, as solubility of solute with solvent.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE[1]

BY F. E. BARTELL AND C. K. SLOAN[2]

RECEIVED DECEMBER 10, 1928 PUBLISHED JUNE 5, 1929

Since the accuracy in measurement of change in concentration by the interferometric method is practically independent of concentration, this method was used to study adsorption from non-aqueous systems over the entire concentration range. A series of dilute solutions of ethyl alcohol in benzene was prepared and adsorption by activated carbon measured (Table I) in the manner described in an earlier paper.[3]

TABLE I

ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

Init. alc. concn., $1 - c_0$	m	Δc	$1 - c$	$N\Delta c/m$	x	$H\Delta x/m$
0.01129	0.1777	0.00054	0.01075	0.0118	0.0180	0.255
.02252	.2349	.00098	.02154	.0158	.0359	.337
.04397	.1987	.00101	.04296	.0195	.0806	.412
.08137	.2575	.00067	.08070	.0099	.1294	.203
.15440	.2308	−.00048	.1549	−.0083	.2370	−.164

First, consider the adsorption of benzene when present in relatively small concentration. When the values of log $H\Delta x/m$ are plotted against log x°,[4]

---

[1] The material presented in this paper is from a dissertation submitted by C. K. Sloan to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928. This paper was presented at a meeting of the Colloid Division of the American Chemical Society at Swampscott, September, 1928.

[2] DuPont Fellow in Chemistry, 1927–1928.

[3] Bartell and Sloan, THIS JOURNAL, 51, 1637 (1929).

[4] The symbols used in this paper are the same as those used in an earlier paper: H = total number of millimoles in solution; x = molar concentration; Δx = change in molar concentration; m = weight of adsorbent; c_0 = initial concentration; c = final concentration; N = amount of solution; and a and n are constants.

a curve is obtained which is decidedly concave toward the concentration axis (Fig. 2). It has been shown that the Freundlich equation must be modified when the adsorption is measured in terms of change in concentration, the modified equation being, $H\Delta x/m = ax^{n}(1 - x)$.

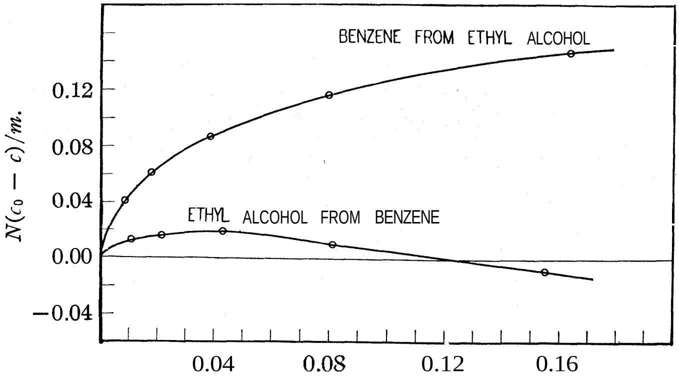


Fig. 1.—Benzene from ethyl alcohol.

The plot of the difference between log Hx/m and log $(1 - x)$ against log x should give a straight line if the adsorption of benzene follows the Freundlich equation and if no solvent is adsorbed simultaneously.

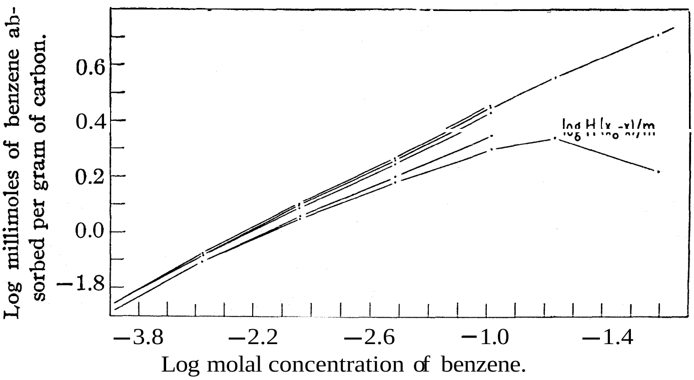


Fig. 2.—Benzene from ethyl alcohol by successive approximations.

A plot of log $H\Delta x/m$ − log $(1 - x)$ against log x gives almost a straight line, though there is still a tendency to concavity toward the concentration axis. This must be due either to a decrease in the adsorption of benzene caused by the presence of ethyl alcohol, or to the fact that simultaneous adsorption of ethyl alcohol and benzene results in a smaller change in concentration than would result if benzene alone were being removed from solution.

An insight into what occurs is obtained by considering the changes in concentration resulting when carbon is added to solutions containing small amounts of ethyl alcohol. The data show that there is an adsorption of ethyl alcohol in this range. This does not mean that benzene is not taken up by the carbon. The number of molecules of benzene adsorbed at the carbon–solution interface may still greatly exceed the number of ethyl alcohol molecules adsorbed, but the fact that a lowering of concentration of alcohol results in the bulk liquid means that a higher concentration of alcohol exists in the adsorbed layer than in the bulk liquid. This process must be classed as selective adsorption of ethyl alcohol, even though actually a greater number of benzene molecules is adsorbed. The plot of $H\Delta x/m$ against the concentration of alcohol $(1 - x)$ gives a curve similar to the curve for adsorption from very dilute solutions. The concavity of the log curve is more pronounced than that representing the adsorption of benzene from dilute solutions in ethyl alcohol. Thus, at about 0.2 mole fraction of ethyl alcohol ($x = 0.8$), carbon produces no change in the concentration of the solution (Fig. **3**). There probably is pronounced adsorption at this point, but the apparent adsorption of each component is zero because the concentration of the adsorbed layer is here the same as that of the bulk liquid.

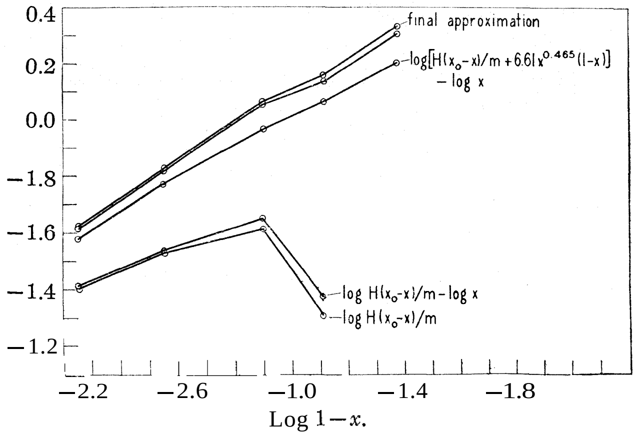


Fig. 3.—Ethyl alcohol from benzene by successive approximations.

Since the apparent adsorption of each component is in accordance with the Freundlich equation when that component is present in low concentration, it is reasonable to suppose that the Freundlich equation would be applicable for the adsorption of each component over a greater concentration range. The change in concentration due to adsorption of benzene can be represented by the following equation

$$H\Delta x_1/m = ax^n(1 - x)$$

Now let us represent the change in concentration due to adsorption of ethyl alcohol by a similar equation

$$H\Delta x_2/m = b(1 - x)^d x$$

The resultant change in concentration will be equal to the difference between these two terms. The decrease in mole fraction of benzene resulting from the simultaneous adsorption of both components is

$$H\Delta x/m = H(x_1 - x_2)/m = ax^n(1 - x) - b(1 - x)^d x$$

After this formula had been derived, it was found that such an equation had been used by Wo. Ostwald[5] to express the results of an experiment of Gustafson, who determined the adsorption from mixtures of acetic acid and phenol, concentrations being expressed in terms of weight rather than mole fraction.

Four points are necessary for the evaluation of the constants of this type of equation. The method of solution is one of successive approximations. Since the adsorption of benzene from dilute solution is governed largely by the first term of the equation, the first approximation for the constants a and n is made by plotting the difference between log $H\Delta x/m$ and log $(1 - x)$ as a function of log x. Since this plot approximates a straight line for small concentrations of benzene, two points are taken for calculation of the constants a and n, using the equation

$$\log H\Delta x/m - \log (1 - x) = \log a + n \log x$$

With this approximation the change in concentration due to adsorption can be represented by the equation

$$H\Delta x/m = 6.61x^{0.465}(1 - x)$$

This equation permits the calculation of the change in concentration due to benzene adsorption at those concentrations where ethyl alcohol is present in small amount. The measured adsorption of ethyl alcohol is then corrected by adding to it this calculated change in concentration due to benzene adsorption. The magnitude of the corrections is shown in Table II.

TABLE II

MAGNITUDE OF CORRECTIONS

EtOH concn.	$1 - x$	0.0180	0.0359	0.0806	0.1294	0.2370
App. ads. of alc.	$-(H\Delta x/m)$	.255	.337	.412	0.203	−0.164
Benzene, ads.	$6.61x^{0.465}(1-x)$	.118	.234	.451	0.802	1.382
EtOH ads., corr.	......	.373	.571	.863	1.005	1.218

These corrected values are now found to be represented fairly well by the Freundlich equation. The constants b and d of the term representing the adsorption of ethyl alcohol are obtained by plotting the difference between the logarithm of the corrected value of alcohol adsorption and log x against log $(1 - x)$. This plot is much nearer a straight line than the plot obtained with uncorrected values of $H\Delta x/m$ (see Fig. 3).

---

[5] Ostwald, *Kolloid-Z.*, **30**, 279 (1922); **32**, 57 (1923); **36**, 289 (1925).

The adsorption of alcohol from benzene can be represented, as a first approximation, by the equation

$$H\Delta x/m = 3.55(1 - x)^{0.550}x$$

This gives a measure of the adsorption of alcohol over all ranges of concentration. The original values for the adsorption of benzene from solutions containing small amounts of benzene can now be corrected. In this case the amount of correction is much smaller, but it does, however, tend to straighten the logarithm curve (see Fig. 2).

The difference in the successive values of the constants becomes so small after a few additional approximations that the accuracy of the experimentally determined values does not warrant further approximation. The successive series of approximations representing the change in concentration due to adsorption of each component is given in Table III. Four additional approximations result in very little change in the values of the four constants. The decrease in concentration of benzene due to adsorption from both dilute and concentrated solutions of benzene in ethyl alcohol, therefore, is obtained by combining the last two terms of the table into a single equation.

TABLE III

SUCCESSIVE SERIES OF APPROXIMATIONS

Adsorption of benzene, $ax^n(1 - x)$	Adsorption of ethyl alcohol, $b(1 - x)^dx$	Adsorption of benzene, $ax^n(1 - x)$	Adsorption of ethyl alcohol, $b(1 - x)^dx$
$6.61x^{0.465}(1-x)$	$3.55(1-x)^{0.55}x$	$8.83x^{0.514}(1-x)$	$5.69(1-x)^{0.648}x$
$8.24x^{0.508}(1-x)$	$4.89(1-x)^{0.615}x$	$9.39x^{0.526}(1-x)$	$6.31(1-x)^{0.668}x$
$8.72x^{0.512}(1-x)$	$5.19(1-x)^{0.627}x$	$9.76x^{0.532}(1-x)$	$6.26(1-x)^{0.662}x$

$$H\Delta x/m = 9.76x^{0.532}(1 - x) - 6.26(1 - x)^{0.662}x$$

The applicability of this equation to adsorption from moderately concentrated solutions is shown by comparison with data giving adsorption of benzene at three such concentrations.

TABLE IV

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

Init. benzene concn., c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2690	0.1682	0.00689	0.2621	0.1548	0.1725	2.213
.5268	.2366	.00612	.5207	.1026	.3907	1.672
.6854	.2193	.00343	.6820	.0573	.5586	1.019

The agreement between experimental values and those calculated by the above equations is shown in Table V and Fig. 4.

Adsorption from the System Ethyl Carbonate-Ethyl Alcohol.—In an earlier paper[3] it was shown that ethyl carbonate is adsorbed from dilute ethyl alcohol solutions. Other measurements were made to determine the adsorption at other concentrations. The results are given in Table VI,

TABLE V

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

x	$9.76x^{0.532}(1-x)$	$6.26(1-x)^{0.662}x$	Diff.	$H\Delta x/m$	Error
0.00513	0.587	0.032	0.555	0.521	+0.034
.01050	0.855	0.065	0.790	0.787	+.003
.02289	1.280	0.141	1.139	1.123	+.016
.04854	1.857	0.294	1.563	1.537	+.026
.1033	2.616	0.602	2.014	2.022	−.008
.1725	3.173	0.953	2.220	2.213	+.007
.3907	3.608	1.761	1.847	1.672	+.175
.5586	3.160	2.034	1.126	1.019	+.107
.7630	2.004	1.841	0.163	0.164	−.001
.8706	1.174	1.406	−.232	−.203	−.029
.9194	0.756	1.097	−.341	−.412	+.071
.9641	0.344	0.667	−.323	−.337	+.014
.9820	0.174	0.430	−.256	−.255	+.001

TABLE VI

ADSORPTION OF ETHYL CARBONATE FROM ETHYL ALCOHOL

c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2781	0.00326	0.2748	0.068	0.129	0.607
.5490	.00173	.5473	.038	.321	.483
.7855	−.00033	.7858	−.007	.589	−.094
.8972	−.00118	.8984	−.030	.775	−.57
.9498	−.00075	.9507	−.020	.883	−.42
.9757	−.00038	.9761	−.010	.941	−.21

The curve representing adsorption over the entire concentration range has an S-shape (Fig. 5). Ethyl carbonate is preferentially adsorbed from solutions which are relatively dilute in ethyl carbonate; whereas ethyl alcohol is preferentially adsorbed from solutions which are relatively dilute

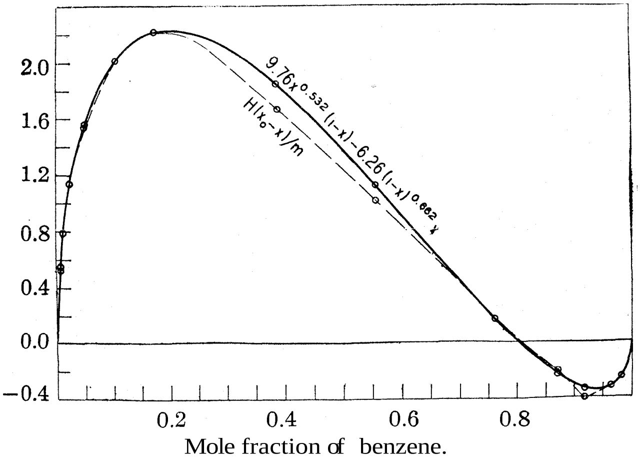


Fig. 4.—Benzene from ethyl alcohol.

in alcohol. The concave nature of the logarithm curve (see Fig. 6) shows how the change in concentration due to adsorption of ethyl carbonate is influenced by the simultaneous adsorption of solvent.

The accuracy in the determination of the change in concentration due to adsorption from this system is not so great as in the other systems investigated. This is due to the fact that there is very little difference between the refractive indices of the two components. This makes impossible an accurate calculation of the constants of the equation representing the adsorption from this system. The two parts of the S-curve are approximately the same. The exponent of the term representing the adsorption of ethyl carbonate is 0.7. The corresponding value for ethyl alcohol is 0.8.

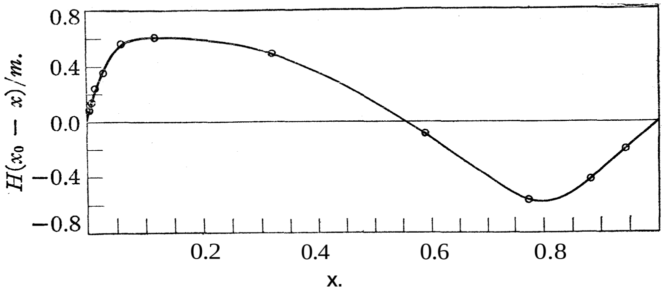


Fig. 5.—Ethyl carbonate from ethyl alcohol.

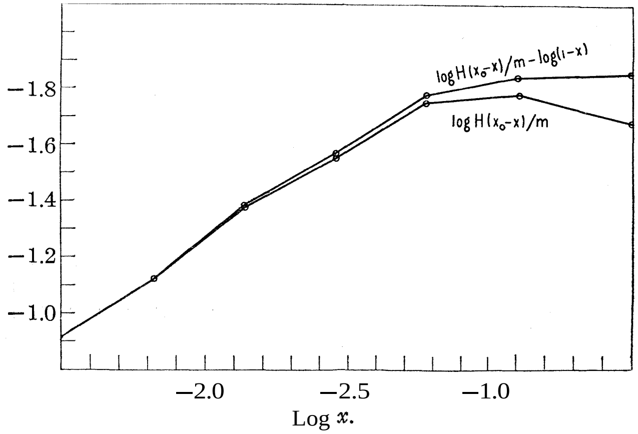


Fig. 6.—Ethyl carbonate from ethyl alcohol.

Adsorption from the System Benzene-Ethyl Carbonate.—The results of adsorption from this system are probably more striking than are those from other systems investigated. The adsorption of one of the components, benzene, conforms to the Freundlich equation up to a very high concentration of that component. This is shown by the fact that the plot

(Fig. 8) of the difference between the logarithms of $H\Delta x/m$ and x against $\log x$ is practically a straight line until x becomes 0.9. As the concentration of benzene is increased further, its adsorption is less than that indicated by the adsorption isotherm. At a molar concentration of 0.995, benzene is even slightly "negatively adsorbed." This statement does not mean that benzene is not adsorbed at this concentration. There is reason to believe that the adsorption of benzene is even greater at this concentration than it is when it is positively adsorbed at a lower concentration. The customary use of the term, negative adsorption, is an unfortunate one. A reader unacquainted with the accepted meaning of this term is led to believe that the other component (ethyl carbonate in this case) makes up the adsorbed layer exclusively. It would be better to speak of this as a preferential adsorption of ethyl carbonate rather than a negative adsorption of benzene. In this system the agreement of the experimentally determined points with the Freundlich equation indicates that the adsorption of ethyl carbonate is comparatively small. The straight portion of the logarithm curve permits

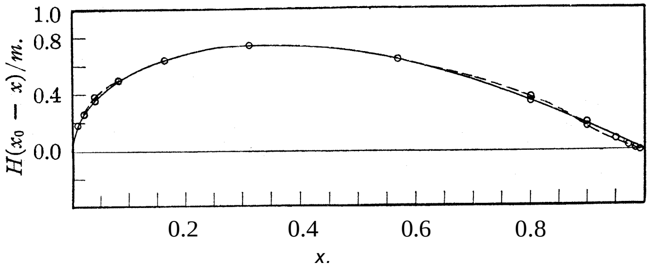


Fig. 7.—Benzene from ethyl carbonate.

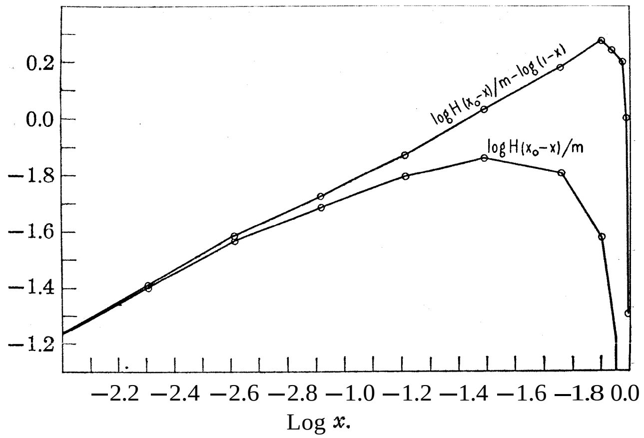


Fig. 8.—Benzene from ethyl carbonate.

a calculation of the constants of the equation representing the adsorption of benzene.

$$H\Delta x/m = 2.01x^{0.535}(1 - x)$$

The agreement between the values calculated using this equation and those experimentally determined is shown in Table VII.

TABLE VII

ADSORPTION OF BENZENE FROM ETHYL CARBONATE

4	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$	$2.01x^{0.535}(1-x)$	Diff.
0.00692	0.1788	0.00053	0.00639	0.0132	0.00961	0.165	0.165	0.000
.01414	.1839	.00053	.01336	,0195	.02006	.248	.243	−.005
.02853	.1811	.00116	.02737	.0290	.04081	.366	.348	−.018
.05808	.1846	.00155	.05653	.0391	.08306	.484	.486	+.002
.1169	.1838	.00211	.1148	.0515	.1640	.621	.638	+.017
.2330	.1917	.00281	.2302	.0649	,3113	.741	.741	.000
.4705	.3444	.00499	.4655	.0631	.5683	.642	.642	.000
.7295	.2111	.00209	.7274	.0403	.8014	.375	.354	−.021
.8590	.2061	.00096	.8580	.0185	.9013	.165	.188	+.023[a]
.93055	.2042	.00045	,93010	.0086	.9526	.075	.093	+.018[a]
.96648	.2240	.00015	.96633	.0027	.9775	.022	.045	+.023[a]
.98406	.2321	.00002	.98404	.0003	.9894	.002	.021	+.019[a]
.99243	.2072	−.00004	.99247	−.0007	.9950	−.007	+.010	+.017[a]

[a] Indicates small adsorption of ethyl carbonate.

Adsorption from the System a-Bromonaphthalene-Benzene.—The adsorption from this system is shown in Table VIII and Figs. 9 and 10.

TABLE VIII

ADSORPTION OF α-BROMONAPHTHALENE FROM BENZENE

c	0.01077	0.02401	0.04844	0.0972	0.1928	0.3570	0.6294	0.99034
$N\Delta c/m$	.0491	.0668	.0796	.0929	.0990	.0811	.0122	−.0057
x	.00409	.00919	.01883	.0390	.0826	.1732	.3903	.9748
$H\Delta x/m$	.239	.328	.396	.478	.543	.504	.097	−.022

Here, again, the adsorption curve is S-shaped. The component, α-bromonaphthalene, having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. The decrease in concentration of a-bromonaphthalene due to adsorption from this system is given fairly well by the equation

$$H\Delta x/m = 2.86x^{0.445}(1 - x) - 4.54(1 - x)^{1.05}x$$

Adsorption from the System a-Bromonaphthalene-Ethyl Carbonate.—In this system, as in others, the adsorption of the component having the higher adhesion tension is the greater. The adsorption curve has the usual characteristics.

Application of the **Gibbs Equation to Adsorption at** the **Carbon–Solution** Interface.—The results of these experiments indicate that the substance

TABLE IX

ADSORPTION OF α-BROMONAPHTHALENE FROM ETHYL CARBONATE

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.10015	0.0860	0.00137	0.00878	0.0774	0.00519	0.388
.02124	.1339	.00290	.01834	.1009	.01091	.508
.04404	.1025	.00262	.04142	.1185	.0249	.604
.08955	.1049	.00293	.08662	.1292	.0530	.670
.1744	.1188	.00333	.1711	.1322	.1086	.711
.3327	.1369	.00318	.3295	.1183	.2262	.687
.6006	.1068	.00112	.5995	.0607	.4695	.403
.99146	.1546	−.00008	.9916	−.0034	.9871	−.025

having the higher adhesion tension will be the one which will be adsorbed to the greater extent. No one component of a binary system, however, is preferentially adsorbed over the entire concentration range. From each of the systems investigated, the substance of lower adhesion tension is adsorbed if it be present in sufficiently low concentration in solution. This gives rise to the so-called S-shaped adsorption curve. This is in agree-

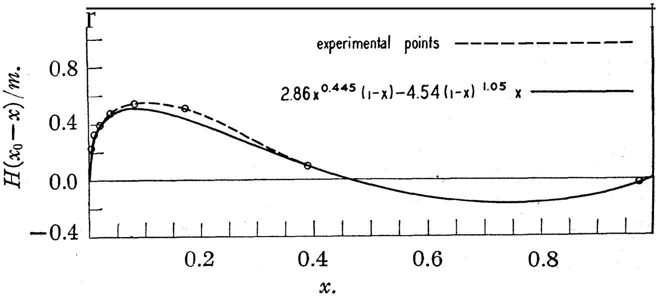


Fig. 9.—α-Bromonaphthalene from benzene.

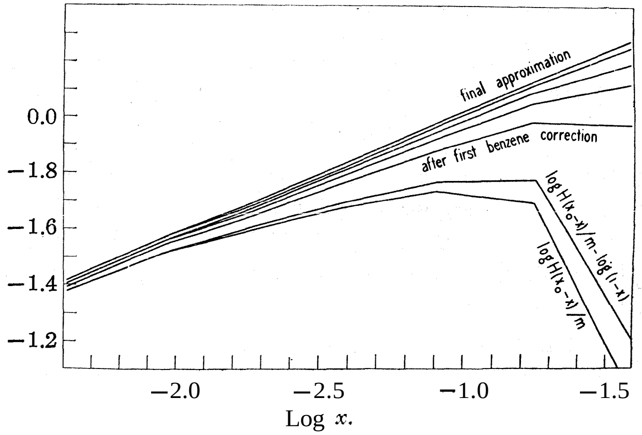


Fig. 10.—Adsorption of α-bromonaphthalene from benzene by successive approximations.

ment with the work of Williams,[6] who considered it justifiable to assume a minimum in the solid–liquid interfacial tension–concentration curve. Williams contended that the results obtained by Dora Schmidt-Walter[7] and Gustafson[8] indicating negative adsorption could be explained on the basis of the Gibbs adsorption equation[3] by considering that the addition of either component to the other which is in contact with a carbon surface will result in a lowering of the interfacial tension at the carbon–liquid interface. Although there is no method for a direct measurement of these interfacial values, the existence of such minimum points is not improbable. It has been shown that, for most binary systems, the surface tension-concentration curve does have a minimum point.[10] If the Gibbs adsorption formulation holds, the results of the experiments herein described point to a more pronounced minimum point in the interfacial tensions between a solution and carbon than between a solution and air. If the method of

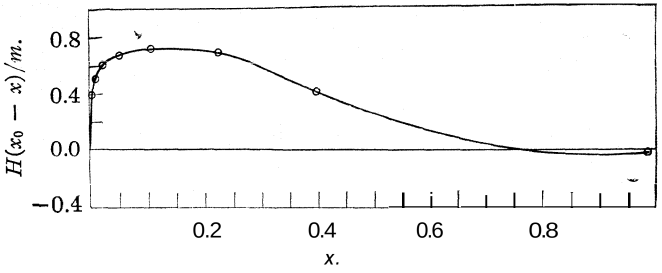


Fig. 11.—α-Bromonaphthalene from ethyl carbonate.

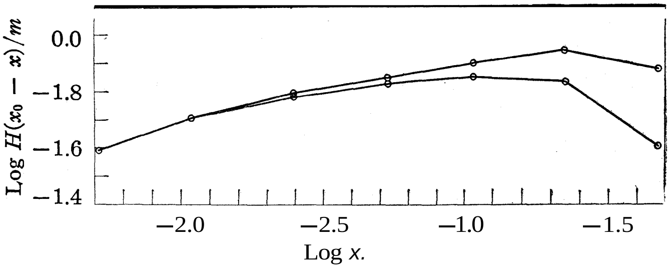


Fig. 12.—a-Bromonaphthalene from ethyl carbonate.

---

[6] Williams, *Medd. Vetenskapsakad* Nobelinst, (2) Nr. 27 (1913) (see Freundlich, "Colloid and Capillary Chemistry," p. 179); Proc. Roy. *Soc. Edinburgh*, **37**, 161 (1916); 38, 24 (1917); 39, 48, 52 (1918); *Proc.* Roy. *Soc. London*, **96A**, 287, 298 (1920).

[7] Schmidt-Walter, *Kolloid-Z.*, 14, 242 (1914).

[8] Gustafson, *Z. physik.* Chem., *91*, 385 (1916).

[9] Reference is here made to the rather generally used adsorption equation, $u = -(c/RT) \times dS/dc$, which has been developed from the thermodynamic rule of Gibbs relating change of concentration in the boundary layer and surface tension or interfacial tension. For lack of a better designation, this will be referred to as the Gibbs equation.

[10] Freundlich, "Colloid and Capillary Chemistry," p. 53.

Bartell and Osterhof[11] can be extended so as to measure the adhesion tension value of a binary liquid mixture against a solid, it is believed that a rigorous test can be made of the Gibbs formulation. Adhesion tension is defined by the following equation, $A_{12} = S_1 - S_{12}$. It follows that the sum of the value of the adhesion tension A_{12} and interfacial tension of a liquid against the same solid, S_{12}, must be equal to the surface tension of that solid S_1 (this latter value being constant). A change in the value of the interfacial tension with concentration at the solid–liquid interface is equal and opposite in sign to the corresponding change in adhesion tension.

$$\mathrm{d}A_{12}/\mathrm{d}c = -\mathrm{d}S_{12}/\mathrm{d}c$$

The Gibbs equation, $u = (-c/RT) \times dS_{12}/\mathrm{d}c$, then becomes

$$u = +\frac{c}{RT} \times \frac{\mathrm{d}A_{12}}{\mathrm{d}c}$$

Corresponding values of $\mathrm{d}A_{12}/\mathrm{d}c$ (adhesion measurements of solutions) and of u (interferometric measurement of change in concentration due to adsorption) should afford a test of the Gibbs formulation. Such a test has been lacking heretofore because no reliable data could be obtained for the values of both u and $\mathrm{d}S_{12}/\mathrm{d}c$ at a single interface. This correlation should establish the importance of certain factors which are disregarded by the usual formulation of the Gibbs principle. These factors include: the change of thermodynamic potential due to adsorption of solvent as well as that of solute, electrical properties of the boundary layer and the deviation of the osmotic pressure from the ideal state.

Determination of Total Adsorption.—Williams[6] realized that the measurement of the change in concentration gives only the apparent adsorption. He attempted, therefore, to obtain a second independent equation for the adsorption of each component by measuring the amount of each which is adsorbed by carbon from the vapor phase. The attainment of equilibrium in this latter procedure is not easy, as is shown by the recent work of Tryhorn and Wyatt[12] and Gustafson.[8]

Bakr and King,[13] working with a benzene-iodine-carbon system, and Bakr and McBain,[14] working with toluene and acetic acid, appear to have been successful in obtaining adsorption data for both solute and solvent for systems in equilibrium.

The fact that the change in concentration can be expressed quite accurately by a combination of two adsorption isotherms makes possible a calculation of the absolute adsorption of each component. If the equation $H\,\Delta x/m = ax^n(1-x) - b(1-x)^d x$ holds over the entire concentration

---

[11] Bartell and Osterhof, *Z. physik. Chem.*. 130, 715 (1927); *Ind. Eng. Chem.*, 19, 1277 (1927).

[12] Tryhorn and Wyatt, *Trans. Faraday Soc.*, 21, 399 (1927); 22, 134, 139 (1927); 24, 36 (1928).

[13] Bakr and King, *J. Chem. Soc.*, 119, 454 (1921).

[14] Bakr and McBain, THIS JOURNAL, 46, 2718 (1924).

range, ax^n and $b(1-x)^d$ are the respective weights of the solute and solvent adsorbed; a is the weight of solute adsorbed from pure solute. The fact that the value of a for a given solute does vary somewhat for the given solute means that the solute adsorption may be cut down to some extent by the presence of solvent. The results of Gustafson and of Bakr and McBain also indicate this. As the concentration of solute becomes large, the term $(1-x)$ decreases and the change in concentration due to solute adsorption becomes small. Even though the value of a is lower than the weight taken up from pure solute, it may still be used to represent the adsorption from the more dilute solutions.

In this investigation adsorption is expressed in terms of $H\Delta x/m$. In order to express the apparent adsorption more accurately, the change in concentration should be multiplied by the number of millimoles of solution after adsorption rather than the number before (H). Measurements indicate that as much as 5% of the solution may be adsorbed. The change in the value of H may therefore be quite appreciable unless relatively constant amounts of carbon and solution are used. A series of adsorption curves could be obtained over a limited range of concentration (about 50%) by using different amounts of carbon. If, for a given value of x, the value of $H\Delta x/m$ varies with the amount of carbon added, it will permit a calculation of the change in the value of H. This change represents the true total molecular adsorption.

Adsorption by Silica.—The measurements of Bartell and Osterhof[11] indicate that the order of the adhesion tension of different liquids against silica is opposite to the order against carbon. Thus benzene has a high adhesion tension against carbon, whereas the corresponding value against silica is low. On the other hand, the adhesion tension of ethyl carbonate is relatively low against carbon and high against silica. Since the adsorption from a binary system by carbon has been found to be dependent on the adhesion tension of the components against carbon, it is reasonable to expect that the adsorption by silica would be dependent on the corresponding adhesion tension values against silica. Thus, ethyl carbonate should be adsorbed by silica to a greater extent than benzene from solutions containing these two substances, inasmuch as the adhesion tension of the ethyl carbonate against silica is greater than that of benzene. This has been found to be the case. The results of measurements of adsorption by silica from this and other systems will be reported in a future paper. In each of the systems investigated the adsorption curve is S-shaped and the carbon and silica curves are quite opposite in nature.

Summary

The interferometric method is used to measure the adsorption by carbon from a number of binary non-aqueous systems over the entire concentration

range. In each case the adsorption curve is S-shaped. The component having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. When the component of lower adhesion tension is present in very low concentration it is, however, preferentially adsorbed.

An equation

$$H\,\Delta x/m = ax^n(1 - \mathrm{X}) - b(1 - x)^d x$$

is used to represent the preferential adsorption over the entire concentration range. The derivation of this equation is made on the assumption that the adsorption of each component follows the Freundlich equation.

It is pointed out that the adsorption at a given interface must depend on the rate of change of that particular interfacial tension with the concentration of the bounding phases. The importance of the measurement of adhesion tension values of solutions is pointed out since the rate of change of adhesion tension is equal and opposite in sign to the rate of change of interfacial tension with concentration.

The Gibbs principle is restated in terms of adhesion tension rather than interfacial tension. *"There will be an excess in the concentration of the solute in the interfacial layer if the rate of change of the adhesion tension of the solution against the adsorbent is positive."* It is pointed out that the usual formulation of the principle of Gibbs does not take into consideration a number of existing factors. It is felt that a correlation of the data from adsorption and adhesion tension measurements will permit a more complete formulation of this principle.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KANSAS]

A MODIFICATION OF THE MOVING BOUNDARY METHOD FOR THE DETERMINATION OF TRANSFERENCE NUMBERS

BY H. P. CADY AND L. G. LONGSWORTH

RECEIVED JANUARY 4, 1929 PUBLISHED JUNE 5, 1929

Introduction

An adaptation of the method of moving boundaries for the determination of transference numbers, involving two differences from recent procedure, has been developed and studied by the authors. The novel features are, first, a single ascending boundary only is observed and, second, a metal anode soluble under the action of the electric current is the source of indicator ions. For example, metallic silver was electrolyzed into a solution of potassium nitrate. Under the conditions of the experiment, this silver furnishes silver nitrate which serves as the indicating electrolyte for the potassium ion constituent of potassium nitrate. The necessity of previous adjustment of the concentration of the indicator electrolyte is thus avoided and no special mechanism is required in the initial formation of the boundary. It was the object of this research to determine the effect of the various factors involved on the stability and velocity of the boundary thus produced.

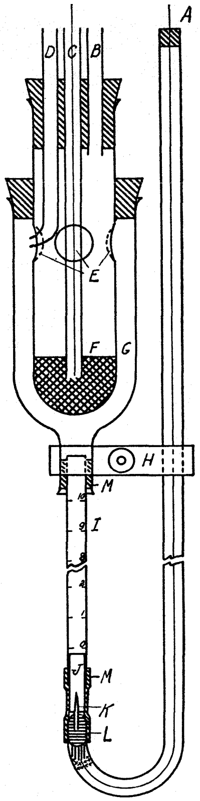


Fig. 1.—Moving boundary cell. *A*, Anode lead; B, vent tube; *C*, cathode lead; D, tube for filling cell; E, holes in cathode tube; F, cathode, lead dipping in paste of PbO_2 and H_3BO_3; G, cathode chamber; *H*, clamp; **I**, graduated tube in which boundary ascends; *J*, cylindrical metal anode; *K*, platinum tip sealed in tube leading anode connection out of thermostat; L, mercury globule making contact with platinum tip and anode held in place by de Khotinsky cement; ***M***, rubber connections.

Apparatus and Method

(a) The Cell.—The apparatus used is shown in Fig. 1. The cylindrical metal anode, J, is machined to fit the graduated and calibrated tube, I, in which the boundary is developed and moves. This anode fits the tube rather snugly and is wedged onto the platinum tip sealed into the glass tube leading the anode connection out of the thermostat. The general design of the cathode chamber is as described by MacInnes and Brighton,[1] and is arranged to have the cathode at some distance from the calibrated tube in which the boundary ascends. The cathode is designed so as to avoid influences which might disturb the progress of the boundary in the graduated tube.[2]

The assembled cell is then mounted in a thermostat furnished with parallel plate glass sides and equipped with the optical system whose profile is shown in Fig. 2. The microscope, F, contains a scale in the eyepiece and is of such depth of focus as to have the tube in which the boundary moves within its focal range.[3] The frosted glass background, H, was illuminated from behind and the narrow black screen, I, on this background, together

---

[1] MacInnes and Brighton, This journal, 47, 994 (1925).

[2] A cylinder of fused silver chloride with a helix of silver wire as core was used with equal success.

[3] In order to locate the boundary with respect to the graduations on the tube, the virtual image, K, of the dark-light margin, I, must be near enough to the graduated tube so that it also comes within the focal depth of the microscope. This may be accomplished by moving the screen and background, H, I, in closer to the moving boundary cell or by working with higher concentrations in the moving boundary cell. The first expedient, however, reduces the sensitivity of this means of detecting the boundary, and the second necessitates the use of solutions of such concentrations as are almost outside the range of the method as developed thus far. With certain solutions of the alkali acetates in anhydrous acetic acid as solvent, it has been found possible to use a microscope in this manner and to a very marked advantage, but for most of the work in water where the concentrations varied from 0.2 to 0.02 *N* it was found necessary to dispense with the microscope and this was replaced by a tube with rectangular openings at either end—merely to insure uniform line of sight in locating the boundary.

with the microscope carriage, E, were arranged on threaded rods, D, provided with bevel pinions, B, so that the two could be raised or lowered together.

The source of potential for these experiments has been four hundred volts of storage "B" batteries. The current in the circuit was maintained constant throughout any given experiment by hand regulation of a rheostat in series with the moving boundary cell and the source of potential. The value and constancy of this current was ascertained by means of a potentiometric determination of the potential drop across a standard resistance inserted in the circuit.

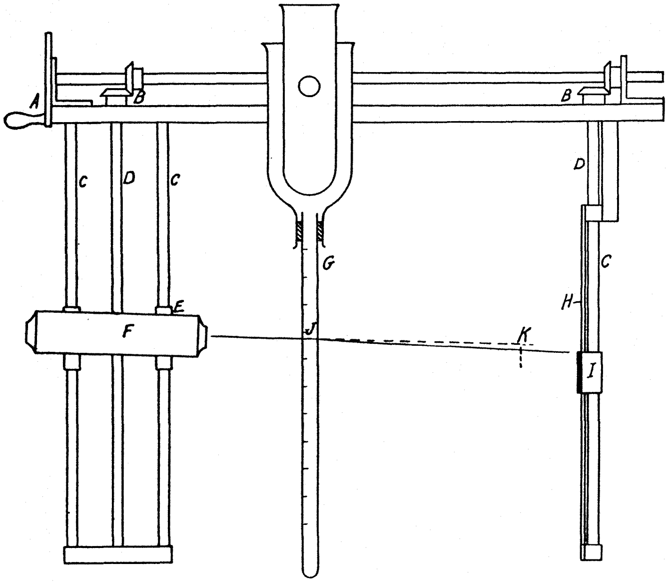


Fig. 2.—Profile of optical system. *A*, Crank; B, bevel pinions; *C*, guide rods; D, threaded rods; E, microscopic carriage; *F*, microscope; G, moving boundary cell and tube; *H*, ground glass background—illuminated from behind; *I*, movable opaque screen; *J*, position of margin; K, refraction (?) image of upper edge of I.

The tube was graduated as described by MacInnes, Cowperthwaite and Huang,[4] and is calibrated for total volume between the first and last marks only[5] by means of mercury and a dividing engine. The boundary is caused to sweep through the entire volume between these marks and the intermediate marks were used to ascertain the constancy of the boundary velocity under a constant potential gradient. Such constancy is one criterion of a properly functioning boundary.

(b) Location and **Visibility** of **the** Boundary.—The boundary we are dealing with in this research is the liquid junction between the solution of electrolyte originally placed in the cell and the ever-increasing column of heavier electrolyte having a common anion and an unlike cation formed from the metal anode. The characteristics which this in-

---

[4] MacInnes, Cowperthwaite and Huang, THIS JOURNAL, 49, 1710 (1927).

[5] The uniformity of bore was not determined directly but the boundary velocities indicated that all of the tubes employed, save one, were sufficiently uniform.

dicator cation must have are described in detail by Franklin and Cady[6] in their article on ion velocities in liquid ammonia.

A necessary condition for a visible boundary is a difference in refractive indices of the two solutions of electrolytes meeting at the boundary. Due to this difference of refractive index the upper edge of the movable opaque screen on the illuminated background (see Fig. 2) will appear distorted when in line with the boundary; this distortion serves as a means of locating the boundary. However, the visibility of a boundary seems to depend also on a sharpening[7] produced by the sudden change of the potential gradient at the boundary as well as on the difference in the refractive indices. Thus cadmium nitrate as indicator electrolyte formed by electrolysis of metallic cadmium into 0.1 N potassium nitrate gave more distinct boundaries than did either lead or silver nitrate—due to its relatively high specific resistance, though the difference in refractive index at the boundary would favor the other indicator electrolytes.

Consideration of Factors Affecting the Results

The expression, $T_c = (LCFA)/(1000IT)$, correlating the quantities determined in a single boundary experiment with the transference number of the given ion constituent has been derived by a number of investigators. In this expression the symbols have the following significance. The boundary travels L centimeters in T seconds in a tube whose (uniform) average cross-sectional area is A square centimeters. I is the current in amperes flowing in the tube. C is the number of equivalents per liter of solution of electrolyte originally placed in the tube and F is the Faraday in coulombs. The ratio L/T thus corresponds to the boundary velocity when the current, and hence the potential gradient, is maintained constant. The various quantities measured and the factors influencing the motion of the boundary are discussed in the following.

(a) The Concentration Range Studied.-Sharp and easily visible boundaries were obtained with potassium nitrate at 0.02, 0.1, 0.2 and 1.0 N with either lead or silver as indicator ion at the three lower concentrations and silver only at the higher concentration. In the 1.0 N solution the formation of ions at the silver anode could not be made to proceed smoothly for any great period of time and oxygen evolution would usually destroy the boundary after it had risen two or three centimeters from the face of the electrode. Also, convection currents in the indicator solution at this concentration are marked and their disturbing effect on the boundary velocity probably renders concentrations of this magnitude outside the range of the method in its present state of development—at least, in tubes of the size employed.

(b) Tube Area.—Boundaries with 0.1 N potassium nitrate were run in four sizes of tubes, their average cross-sectional areas being 0.1934, 0.1102, 0.06702 and 0.03909 sq. cm., respectively. Both silver and lead anodes were used as sources of indicator ions and a variety of potential gradients employed. In the two larger tubes the measured values of the transference numbers were found to be independent of the tube area whereas in the two smaller tubes these values decreased with the size of the tube—the measured transference number in the smallest tube being about 0.8% lower than the values obtained in the two largest tubes.

These results are recorded in Table I.

---

[6] Franklin and Cady, **THIS JOURNAL,** 26,499 (1904).

[7] MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15**, 18 (1929).

y

TABLE I

EFFECT OF TUBE AREA

Measured transference number of the potassium-ion constituent of 0.1 N potassium nitrate at 25°.

Anode	Ag	Pb	Pb	Ag	Pb	Ag
Tube area	0.1934	0.1934	0.1102	0.06702	0.03909	0.03909
Poten. grad., v./cm.	8.615	12.92	Table II	12.34	12.69	10.57
T_c	0.5122	0.5123	0.5121	0.5096	0.5089	0.5076

The possibility of electro-endosmotic forces affecting the boundaries in small-bore tubes has been suggested by Dr. D. A. MacInnes.

(c) Potential Gradient.—The simple theory requires the measured transference number to be independent of the potential gradient. This was tested by making several series of runs over a considerable range of potential gradients. The results of one such set of determinations are recorded in Table II.

TABLE II

EFFECT OF POTENTIAL GRADIENT

Measured transference number of the potassium-ion constituent of 0.1 N potassium nitrate at 25° with a lead anode as the source of indicator ions.

Tube area, sq. cm.	0.1102	0.1102	0.1102	0.1104	0.1102	0.1102	0.1102
Poten. grad., v./cm.	3.781	7.562	11.34	11.34	15.12	18.91	22.69
T_c	0.5119	0.5121	0.5120	0.5122	0.5151	0.5165	0.5228

All values for the transference numbers have been corrected for the volume changes at the electrodes as described by Lewis.[8] The constant value obtained at low potential gradients (T_c = 0.5120) is in good agreement with that of MacInnes, Cowperthwaite and Blanchard[9] (T_c = 0.5122) obtained from observations on descending boundaries.

Table II serves to illustrate a rather significant feature of the method, namely, the range of potential gradient over which the transference number is independent of that gradient. The range over which the measured transference number is independent of the potential gradient is greater the smaller the cross-sectional area of the tube.

(d) Metals Used as Indicators.—Cadmium, used as a source of indicator ions for the potassium ion constituent of potassium nitrate, did not electrolyze smoothly and values obtained by its use are somewhat inconsistent and persistently low, due probably to secondary electrode reactions producing faster ions that forged ahead of the ions under observation, thus slowing up the boundary. Cadmium, however, electrolyzed very smoothly in halide solutions and gave consistent values for the transference number of the potassium ion constituent of potassium chloride and bromide, respectively. The values obtained, while differing but slightly from the accepted values, will not be quoted here. They probably do not

---

[8] G. N. Lewis, THIS JOURNAL, 32, 862 (1910).

[9] MacInnes, Cowperthwaite and Blanchard, *ibid.*, 48, 1909 (1926).

represent the accuracy of which the method is capable since two refinements, automatic current control and elimination of vibration, were not made in the prosecution of this research.

The value of the measured transference number quoted in Table II is that obtained from the time required for the boundary to travel the full ten centimeters. At high potential gradients, however, time readings per centimeter showed that the boundary was being accelerated, even when acted upon by a constant potential gradient. The initial velocity obtained by graphical methods gave a value of T_c much nearer the constant value obtained at low potential gradients. The lower limit of potential gradient seems to be determined by the sensitivity of the optical system employed and by the sharpening effect of the potential gradient change at the boundary. On the other hand, the upper limit is controlled almost entirely by the convection currents in the indicator solution due to the larger quantity of heat developed in this portion of the tube. It should be noted that long before convection currents become sufficiently vigorous to destroy the boundary entirely, it has become quite convex and its velocity is no longer an indication of the true velocity of the preceding ion constituent.

Automatic Concentration Adjustment

According to Kohlrausch[10] the concentration of the indicator ion will be automatically adjusted to the relation, $C/C' = T_c/T'_c$, where C and T_c are the concentration and cation transference numbers of the solution under observation and the primed symbols the corresponding quantities for the indicator solution.

Two methods of attack have been employed in ascertaining to what extent this concentration adjustment was automatically made. The first depends on the fact that the total resistance of the cell increases as the boundary ascends the tube, since the indicator ions have lower mobilities than the ions they are replacing. The rheostat resistance in the circuit must, therefore, be continually decreased in order to maintain the current constant. The rate of this decrease is a direct indication—except for the effect of the diffusion layer at the electrode—of the velocity of the indicator ion constituent and hence, indirectly, its transference number. If we take the anode as the origin, the length of the tube as L, and the position of the boundary as x, the total resistance of the tube is

$$R = \frac{L - x}{KA} + \frac{x}{K'A}$$

The dimensions of the cathode chamber permit the resistance of this portion to be neglected. The variation of the total resistance with the position of the boundary is

$$\frac{dR}{dx} = \frac{1}{K'A} - \frac{1}{KA}$$

---

[10] **Kohlrausch,** *Ann. Physik,* **62,209** (1897).

from which

$$K' = \frac{K}{1 + KA\dfrac{dR}{dx}}$$

where K is the specific conductance of the solution under observation and K' the corresponding quantity for the indicator solution. *A* is the cross-sectional area of the tube. Hence if we know K' as a function of C', we can determine C'. The values of C' were read directly from a plot of K' against C' and the error involved in this procedure may be rather large since conductance data on some of the electrolytes under consideration at 25° are not very concordant. The effects of the formation of a diffusion layer, to be discussed, and of convection, are both to reduce the measured value of dR/dx. We therefore use the highest value obtained in any given series of runs, this maximum occurring at fairly low potential gradients. According to the equation, C/C' should equal T_c/T'_c. By means of the values of C' obtained as just described, we can determine with the aid of the transference numbers in the literature whether adjustment to the conditions predicted by Kohlrausch has been made. These computations are made in Table III.

TABLE III

CONCENTRATION ADJUSTMENT

Solution	Indicator	C	C′	T_c	T_c	C/C'	T_c/T'_c
KNO_3	Pb	0.0997	0.0961	0.512	0.487	1.04	1.05
KNO_3	Ag	.0997	.0932	.512	.468	1.07	1.09
KCl	Cd	.1000	.0891	.492	.431	1.12	1.14
KBr	Cd	.1008	.0925	.485	.432	1.09	1.12

The ratios, C/C' and T_c/T'_c, given in the last two columns should be the same for each salt measured. The fact that they are nearly so indicates that automatic "adjustment" is attained by the method described in this article. The ratio C/C' is, however, consistently slightly lower than T_c/T'_c. This may arise from the fact that there is a diffusion layer next to the electrode which has the effect of making the concentration appear too high.

The second method consisted in directly measuring the conductance between two platinized platinum tips sealed in the side of the tube. Such measurements were made before and after the boundary had moved by them. The concentration, C', was then interpolated from existing con-

TABLE IV

CONCENTRATION ADJUSTMENT

Solution	Indicator	C	C′	T_c	T'_c	C/C'	T_c/T'_c
KNO_3	Pb	0.1004	0.0932	0.512	0.487	1.07	1.05
KNO_3	Ag	.1004	.0909	.512	.468	1.10	1.09
KCl	Cd	1000	.0873	.492	.431	1.14	1.14
KBr	Cd	.1008	.0912	.485	.432	1.10	1.12

ductance data as has been described in the previous paragraph, and used to test whether "adjustment" had been attained. The results of our measurements by this method are recorded in Table IV.

The values of T_c and T'_c employed in Tables III and IV are those of MacInnes and co-workers where available; otherwise they are taken from the compilation of Noyes and Falk. In all cases they are values at the nearest concentration and temperature to those of the experiment which are available.

This method, which is more nearly independent of errors due to the diffusion layer just mentioned, shows even better concordance between the ratios C/C' and T_c/T'_c.

The Diffusion Layer

For each Faraday of electricity passed through the cell, one gram equivalent of metallic ion is formed at the anode by the electrochemical reaction there. However, only T'_c equivalents are carried away from the electrode by electrolytic migration. Thus $(1 - T'_c)$ equivalents of indicator electrolyte is left in the neighborhood of the electrode. Hence, there is a diffusion layer of indicator electrolyte, of higher concentration than the adjusted value, C', formed at the anode. Our observations and computations[11] from existing theory both show that under the conditions of the experiment pure diffusion will at no time alter the adjusted concentration of the indicator solution immediately behind the boundary. If, however, the convection currents developed in the column of indicator electrolyte penetrate and disturb this diffusion layer, this excess electrolyte will be partially distributed throughout the region of the indicator column. If we can utilize the experience of Smith and MacInnes,[12] which tends to show that an indicator electrolyte concentration greater than C' causes the boundary to move too rapidly, this would explain the high values shown by T_c in Table II at high potential gradients.

In conclusion a word should be said as to the range of the method. With lead and silver as sources of indicator ions the electrolytes to be observed would be restricted to those whose anions give soluble salts with these two metals—which greatly restricts the field—but with cadmium as a source of indicator ions the halides and several other anions are possible but the cations must not be too heavy. Metallic thallium has been made to serve as indicator ion for one of the faster cations in some work in anhydrous acetic acid as solvent. Amalgam electrodes and electrodes of the second class, that is, reversible with respect to the anion, have been investigated to a certain extent and their use would still further extend the range of the method.

[11] Sand, *Phil. Mag.*, **6**, 1, 45 (1901).

[12] Smith and MacInnes, THIS JOURNAL, 46, 1398 (1924).

The authors wish to express their appreciation to Dr. D. A. MacInnes for many helpful suggestions and constructive criticisms in the preparation of this manuscript.

Summary

1. A modification of the moving boundary method for determining transference numbers, in which rising boundaries are used, has been studied. In this new method the boundary starts at the surface of the metal electrode, which furnishes the "indicator" ions by electrochemical solution of the metal.

2. When applicable the new method furnishes a simpler means of obtaining boundaries than has been so far proposed. The method also avoids the necessity of making measurements with indicator solutions of varying concentration, since it has been shown experimentally that there is, with this method, automatic adjustment to the condition, $C/C' = T_c/T'_c$. (C and C', and T_c and T'_c, are, respectively, the normality and cation transference number of the leading and indicator solution.)

LAWRENCE, KANSAS
NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A GRAVIMETRIC AND COLORIMETRIC METHOD FOR THE DIRECT DETERMINATION OF SODIUM

BY EARLE R. CALEY WITH C. W. FOULK

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

It is a curious and interesting fact that no satisfactory method for the direct determination of sodium had ever been produced before the recent appearance of the paper by Barber and Kolthoff,[1] and it is also interesting to note that the present independent experimental study of the same subject had just been completed when the above paper was published. Barber and Kolthoff precipitated the sodium with zinc uranyl acetate. The method described here is analogous but uses magnesium uranyl acetate.[2] The sodium is thrown down as magnesium sodium uranyl acetate, $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2 \cdot (C_2H_3O_2)_2 \cdot 6^1/_2H_2O$, which can then either be dried and weighed or, if small in amount, dissolved in water and measured colorimetrically.

This method, which was first suggested by Streng[3] for the qualitative detection of sodium, was also studied by Miholic[4] and Blanchetière[5] and

---

[1] H. H. Barber and I. M. Kolthoff, THIS JOURNAL, 50, 1625 (1928).

[2] Weiland, *Mitt. Kali-Forsch. Anst.*, **1927**; *C. A.*, **22**, 3600 (1928), used this reagent but gives a formula of the precipitate containing nine molecules of water. We did not have access to his original paper.

[3] A. Streng, *Z. wiss. Mikroskop.*, **3**, 129–130 (1886).

[4] S. S. Miholic, *Bull. Acad. Sci. Zagrab.*, **1920**, 16–23.

[5] A. Blanchetière, *Bull. soc. chim.*, **33**, 807–818 (1923).

later by Barber and Kolthoff, who rejected it partly because of the poor results obtained by other investigators (see paper of Barber and Kolthoff for references) and partly because of their own failure to obtain by its means a precipitate that was stable on prolonged drying. Our own preliminary experiments amply bore out the experience of the previous workers, but fortunately they also suggested the reasons why these early investigators failed to get the desired results. These causes of failure will be given in detail below but they can be summed up here by the general statement that it happened to be a method which required closer attention than is usually given to such details as temperature, stirring and concentration of precipitant. The early investigators failed to consider these points and consequently rarely obtained quantitative results.

A comparison of the Barber and Kolthoff method with the one offered here shows the former to be the more precise if limited to the precipitation of small amounts of sodium (0.008 g. or less) and the latter to be superior in handling larger amounts, up to 0.050 g.

Preparation of the Magnesium Uranyl Acetate.—The following was found to be the most satisfactory method of preparing the reagent.

SOLUTION A		SOLUTION B	
Crystallized uranyl acetate	85 g.	Crystallized magnesium acetate	500 g.
Glacial acetic acid	60 g.	Glacial acetic acid	60 g.
Distilled water	to 1000 cc.	Distilled water	to 1000 cc.

Each solution is separately heated to about 70° until all the salts are dissolved and then the two solutions are mixed at this temperature and allowed to cool to 20°. The large vessel containing the mixed reagent is next placed in water at 20°, and held at this temperature for an hour or two until the slight excess of salts is crystallized out. The reagent is finally filtered through a dry filter into a dry bottle. The solution thus prepared apparently suffers no alteration upon standing and is permanent for all practical purposes when kept away from direct sunlight. A separate portion of some of the first lot of reagent kept in a clear glass bottle exposed to diffused daylight for eight months showed no change in activity or appearance at the end of this time.

General Gravimetric Procedure

The neutral solution containing the sodium, preferably as the chloride, should be reduced to a volume of 5 cc. or less, if there is no separation of salts. A volume of reagent corresponding to the probable sodium content of the solution is then rapidly added and the two solutions are mixed. The flask containing the mixed solution is next partly immersed in a water-bath maintained at 20° and the solution vigorously stirred for thirty to forty-five minutes. The precipitate is then immediately filtered into a Gooch crucible using gentle suction, and after all of the solution has run through the precipitate is washed with successive 5-cc. portions of 95% alcohol. The crucible with its precipitate is finally dried in an air oven at 105 to 110° for thirty minutes and weighed.

The weight of the precipitate, plus one milligram for each 5 cc. of alcohol used in washing, times 0.0153, gives the sodium content of the original solution.

By reason of the large volume and weight of the precipitate formed, 25 mg. of sodium is the maximum amount that should be present, although with care 50 mg. may be determined. In case the amount of sodium present is very small (1 mg. or less) the volume of the solution should be 1 or 2 cc.; otherwise a volume of 5 cc. is used.

Not less than 100 cc. of reagent should be used when the probable amount of sodium is 10 mg. or less. For larger amounts the number of cubic centimeters of reagent should be ten times the number of milligrams of sodium present. An excess of reagent in any case does no harm. It is sometimes necessary to filter the reagent before use if the original filtration was not entirely effective.

A thermostatic control is unnecessary for regulating the temperature at 20°, since a variation of a degree either way does no harm. Indeed, it is only necessary to fill a large vessel with water brought to 19 or 20° and then pay no further attention to temperature control. There is no advantage in working at a lower temperature. The stirring or shaking should be vigorous, since gentle agitation leads to incomplete precipitation.

During filtration the solution should be stirred continually to prevent the crystalline precipitate from adhering to the sides of the flask. The alcohol is preferably delivered from a graduated wash bottle having a fine tip. The first portions should be used to remove the adhering precipitate from the sides of the flask with the aid of a rubber-tipped rod. The end of the washing process is indicated by the wash liquid going through colorless. Ordinarily 20 to 30 cc. of the alcohol is required. A phenomenon that attends the washing of these precipitates should be mentioned because of its deceptive appearance. There frequently appears in the filtrate a precipitate closely resembling that of the triple acetate, which makes it look as though the latter were running through the filter. This precipitation is due to salts thrown out of the concentrated solution by the alcohol.

It is preferable to dry the precipitate at 105° and in no case should the temperature be allowed to rise above 110°, since decomposition begins at a slightly higher temperature.

By reason of the small factor and the slight uncertainty involved in the washing correction, there is no advantage in weighing the precipitate closer than the third decimal place. The use of a washing correction may be eliminated by washing with 95% alcohol saturated with the triple acetate.

Experimental Basis of the Procedure

Causes of the Failure of Previous Investigators.—Preliminary experiments showed that variations of a few degrees in the temperature of the solution had such an effect on the solubility of the precipitate that concordant results could not be obtained without at least a rough temperature control, and, secondly, that above 20° the sodium was not completely precipitated. Since 20° is about the average temperature of a laboratory, low results would be obtained on warm days. The early investigators, evidently unaware of these points, did not control the temperature of their experiments and consequently obtained discordant results, which, as a rule, were too low.

Composition and Properties of the Precipitate.—Streng[3] stated that the triple acetate contained nine moelcules of crystal water, while Miholic[4] found only six. BlanchetiPre[B] on the other hand assumed, without experimental basis, that the precipitate dried at 110° was anhydrous and contained 1.65% of sodium. Our analyses soon showed that this assumption was wrong and that about six molecules of water were retained at 110°. This is in accord with the composition of the analogous and isomorphic sodium uranyl zinc acetate, as found by Barber and Kolthoff. Table I shows the composition of the precipitate formed at 20°.

TABLE I

SHOWING THE COMPOSITION OF A REPRESENTATIVE SAMPLE FROM A MIXTURE OF TWENTY-FIVE PRECIPITATES, ALL OF WHICH HAD BEEN DRIED AT 110°

No.	Uranyl UO_2, %	Magnesium, %	Sodium, %	Acetate radical, %	Water
1	53.77	1.65	1.58	35.79	..
2	53.67	1.65	1.53	35.42	..
3	53.64	1.63	1.58	...	..
4	53.74	1.61	..	...	..
Av.	53.71	1.63	1.56	35.60	7.50
Calcd. compn.[a]	53.79	1.61	1.53	35.26	7.78

[a] The calculated composition is based on the formula, $Mg(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6^1/_2H_2O$.

The values for uranium in the above table were obtained by precipitating the element as ammonium uranate, dissolving and reprecipitating and finally igniting and weighing as U_3O_8. The magnesium was determined by evaporating the filtrate from the uranium precipitate with an excess of sulfuric acid and igniting the mixed sulfates of magnesium and sodium. The magnesium was then determined as the phosphate and after calculating it as sulfate it was subtracted from the mixed sulfates to get the amount of sodium. The acetate radical was obtained by distillation with phosphoric acid and titration of the acetic acid in the distillate with carbonate-free sodium hydroxide. Water was found by difference since the temperature necessary to drive it off caused the decomposition of the material.

These analytical results, it is seen, agree very well with the assumption that the triple acetate has 6.5 molecules of water (see Table I) and contains 1.53% of sodium. This is further confirmed by the numerous analyses made of samples containing known amounts of sodium.

The results in Table I, however, are from a composite sample and since Miholic[4] and Chamot and Bedient[6] have stated that the triple acetates of uranium are of variable composition, it is necessary to offer analyses of a number of individual precipitates. Determinations of uranium and magnesium alone were made since any serious variation in composition would be apparent in these values.

The results of Table II show that the composition of the precipitate is

---

[6] E. M. Chamot and H. A. Bedient, *Mikrochemie*, 6, 13 (1928).

not variable if the conditions of its formation are kept constant as described in the procedure above.

TABLE II

ANALYSES OF SEVERAL INDIVIDUAL PRECIPITATES

Weight of precipitate, g.	0.3212	0.6585	0.9686	1.3002	1.6351	
Uranyl (UO_2), %	53.71	53.60	53.67	53.77	53.57	Av. 53.66
Magnesium, %	1.62	1.58	1.63	1.60	1.64	Av. 1.61

Experiments to determine the proper temperature for drying the precipitate showed that it could be heated for thirty to forty-five minutes at 110° without loss, but a higher temperature or a longer period of heating resulted in decomposition. (Barber and Kolthoff,[1] who also experimented with this precipitate, report that it lost only 0.3% after drying for twenty hours at 110°.) Attempts to ignite the substance to a form suitable for weighing met with failure.

The solubility of the precipitate in 95% alcohol—the most satisfactory washing liquid—was found to be 0.001 g. for each 5 cc. of alcohol used. Since 25 to 35 cc. of alcohol is sufficient for the washing of even a large precipitate, it is seen that this solubility is almost negligible when calculated in terms of sodium. For example, the use of 35 cc. of alcohol corresponds to only 0.0001 g. of sodium.

Effect of Volume of Solution on Completeness of Precipitation.—In the early quantitative work[4] with this method 0.1 N sodium chloride solutions were used, that is, the concentration was kept constant but the volume of the solution varied. Since under practical analytical conditions the opposite is more likely to be true and since, further, a too high dilution of the solution for analysis also dilutes the reagent, the point was studied by making a series of precipitations with varying volumes of sodium chloride solution, all, however, containing the same amount of sodium. The results showed that the volume of the sodium salt[7] solution should not be more than 5 cc. unless between 25 and 50 mg. of sodium were to be precipitated, in which case the volume might be 10 cc., though even in this case 5 cc. would be better.

Amount of Reagent for Complete Precipitation.—Since the reagent is dilute, large volumes must be used for precipitation. The experimental results on this point are presented in Table III.

The above data indicate the importance of having a sufficiently large volume of reagent present to precipitate all of the sodium as triple acetate. The results show that a large volume is required to precipitate the higher amounts of sodium, so much so in fact that the determination of over fifty milligrams of the element renders the method inconvenient and expensive on this account. For practical purposes it would appear that the

---

[7] In these experiments as well as in all subsequent ones the sodium chloride used was purified by several precipitations with hydrogen chloride.

TABLE III

SHOWING THE EFFECT OF VARYING THE VOLUME OF REAGENT

Reagent, cc.	Sodium soln., cc.	Sodium present, g.	Sodium found, g.	Diff., g.
5	2	0.0010	0.0008	−0.0002
10	2	.0010	.0010	.0000
25	2	.0010	.0010	.0000
50	2	.0010	.0011	+.0001
10	2	.0050	.0037	−.0013
25	2	.0050	.0048	−.0002
50	2	.0050	.0050	.0000
75	2	.0050	.0050	.0000
50	5	.0100	.0095	−.0005
75	5	.0100	.0097	−.0003
100	5	.0100	.0097	−.0003
125	5	.0100	.0101	+.0001
75	5	.0200	.0197	−.0003
100	5	.0200	.0198	−.0002
125	5	.0200	.0197	−.0003
150	5	.0200	.0199	+.0001
200	5	.0500	.0486	−.0014
250	5	.0500	.0488	−.0012
300	5	.0500	.0498	−.0002
350	5	.0500	.0496	−.0004
500	5	.1000	.0986	−.0014
600	5	.1000	.0994	−.0006

method is restricted to the determination of small amounts of sodium, which is fortunately the usual case in practice. The uncommonly large volume of reagent required for the complete precipitation of larger amounts of sodium explains in part the failure of previous workers to obtain other than very poor results when working with amounts of sodium in excess of a few milligrams.

Effect of Agitation on Completeness of Precipitation.—As might **be** expected from the complex nature of the triple acetate, its rate of formation is slow. The solutions should, therefore, stand for twenty-four hours or longer before filtering, or they should be stirred or shaken. The latter is obviously the more sensible procedure in these days of motor-driven laboratory equipment.

A series of experiments was made in which sets of 10-mg. portions of sodium as the chloride in 5 cc. of solution were treated with 125 cc. of the reagent. Without agitation, precipitation was far from complete on three hours' standing and even one hour of "gentle" shaking failed to give quantitative results. Thirty minutes of rapid shaking or stirring (motor-driven apparatus) in a flask, however, gave complete precipitation. These experiments disclose still another reason why previous workers had failed to get good results. They all recommend "gentle" stirring or "occasional agitation."

Test of **the** Procedure with Known Amounts of Sodium Chloride.—The results in Table IV were obtained by following the procedure given above.

TABLE IV

A TEST OF THE PROCEDURE WITH KNOWN AMOUNTS OF PURE SODIUM CHLORIDE

Corr. wt. ppt., g.	Sodium found, g.	Sodium present, g.	Diff., g.	Corr. wt. ppt., g.	Sodium found, g.	Sodium present, g.	Diff., g.
0.034	0.0005	0.0005	0.0000	0.966	0.0148	0.0150	—0.0002
.033	.0005	.0005	.0000	1.636	,0250	.0250	.0000
.129	.0020	.0020	.0000	1.660	.0253	.0250	.0003
.129	.0020	.0020	.0000	3.215	.0492	.0500	-.0008
.491	.0075	.0075	.0000	3.261	.0499	.0500	-.0001
.489	.0075	.0075	.0000	3.255	.0498	.0500	-.0002
.969	.0148	.0150	-.0002	3.243	.0496	.0500	-.0004

The results of Table IV show that as much as 50 mg. of sodium can be precipitated successfully. Even the worst case, the fourth from the bottom, would give a satisfactory analytical result on the basis of a one-gram sample (see also Table VII).

Influence of Other Ions.—The results in Table V below were obtained by adding the specified amount of reagent to 5-cc. portions of solution con-

TABLE V

EXPERIMENTS ON PRECIPITATING SODIUM IN THE PRESENCE OF OTHER MEMBERS OF THE ALKALI GROUP

Element	Wt of other element, g.	Reagent, cc.	Sodium present, g.	Sodium found, g.	Diff., g.
K	0.1500	200	0.0200	0.0199	—0.0001
	.2000	200	.0200	.0203	+.0003
	.2500	200	.0200	.0202	+.0002
	.3000	200	.0200	.0218	+.0018
K	.1000	100	.0100	.0101	+.0001
	.1500	100	.0100	.0101	+.0001
	.2000	100	.0100	.0101	+.0001
	.2500	100	.0100	.0103	+.0003
	.3000	100	.0100	.0123	+.0023
	.4000	100	.0100	.0247	+.0147
K	.1000	50	.0050	.0050	.0000
	.2000	50	.0050	.0087	+.0037
	.3000	50	.0050	.0134	3..0084
	.4000	50	.0050	.0194	+.0144
NH_4	.3000	200	.0200	.0200	.0000
	.4000	200	.0200	.0201	+.0001
NH_4	.2000	100	.0100	.0101	+.0001
	.3000	100	.0100	.0100	.0000
	.4000	100	.0100	.0101	+.0001
Li	.0010	100	.0100	.0101	+.0001
	.0030	100	.0100	.0103	+.0003
	.0050	100	.0100	.0107	+.0007
	.0075	100	.0100	.0112	1.0012
	.0100	100	.0100	.0118	+.0018

taining the sodium and another element. The salts (chlorides) of the added elements had been purified until the flame test showed only traces of sodium.

An inspection of these results shows that the ammonium ion is practically without effect on the precipitation. The results for potassium show that under the conditions used no more than 0.25 g. should be present if 100 cc. or more of reagent is employed. With smaller amounts of sodium calling for only 50 cc. of reagent, not more than 0.1 g. is allowable. In such a case, however, more reagent can be used if much potassium is present. The separation from lithium is not good if more than one or two milligrams of that element is present.

The separation from the alkaline earths is presented in Table VI. The experiments were performed as described above for Table V. All of the alkaline earth salts (chlorides) were purified until only spectroscopic traces of sodium remained.

TABLE VI

EXPERIMENTS ON PRECIPITATING SODIUM IN THE PRESENCE OF THE ALKALINE EARTHS AND FERRIC IRON

Element present	Wt. of other element, g.	Reagent, cc.	Sodium present, g.	Sodium found, g.	Diff., g.
Ca	0.3000	100	0.0100	0.0100	0.0000
	.4000	100	.0100	.0101	+.0001
Mg	.3000	100	.0100	.0100	.0000
	.4000	100	.0100	.0101	+.0001
Sr	.3000	100	.0100	.0102	+.0002
	.4000	100	.0100	.0100	.0000
Ba	.3000	100	.0100	.0105	+.0005
	.4000	100	.0100	.0105	+.0005
Fe	.3000	100	.0100	.0101	+.0001
	.4000	100	.0100	.0100	.0000

It is seen that the presence of alkaline earths has no effect on the separation. The high results in the presence of barium were found to be due to traces of sulfate ion in the reagent, which precipitated barium sulfate.

No quantitative experiments were carried out in which sodium was precipitated in the presence of cations other than those recorded above, but this would hardly be necessary because these ions can be removed easily from the solution. Phosphoric acid would obviously interfere and should be removed before attempting to precipitate the sodium.

A Practical Analytical Test.—An important test of a new method is, of course, that of using it in the analysis of some commercial materials the composition of which has been obtained by other methods in competent hands. That test was applied to this method by using it in the determination of sodium in several samples obtained from the U. S. Bureau of Standards. These were Standard Samples No. 88, a Dolomite; No. 70, a Feldspar; and No. 80, a Lime-Soda Glass.

The dolomite was analyzed by treating a one-gram sample with hydrochloric acid and decomposing the insoluble residue by two evaporations with hydrofluoric and sulfuric acids. The two portions were united and evaporated to dryness. The residue was dissolved in hot water, evaporated to 50 cc. and the sodium precipitated as described in the procedure above. A half-gram sample of the feldspar was decomposed by the J. Lawrence Smith method, which was followed up to and including the extraction of the sintered mass with water. This water extract was then acidified with hydrochloric acid and evaporated to dryness. The residue was next dissolved in 5 cc. of water and the sodium precipitated.[8] The lime–soda glass was decomposed with hydrofluoric and sulfuric acids, 0.3000-g. to 0.0400-g. samples being used. The sulfates so obtained were extracted with water and the sodium was precipitated in the solution. The results of these determinations are given in Table VII.

TABLE VII

ANALYSES OF BUREAU OF STANDARDS SAMPLES BY THE DIRECT METHOD FOR SODIUM

No.	Sample	Method of solution	Na_2O, (B. of S.), %	Na_2O by new *method, %	
88	Dolomite	Dec. with HCl, H_2F_2 and H_2SO_4	0.08	0.09	0.09
70	Feldspar	J. Lawrence Smith method	2.38	2.32	2.33
80	Glass	Dec. with H_2F_2 and H_2SO_4	16.65	16.79	16.61

The values in Table VII compare favorably with the Bureau's results and were obtained in far less time than the standard methods require.

The Colorimetric Estimation of Sodium

The triple acetate precipitate is readily soluble in water and, since the resulting solution is colored yellow by the uranium compound present, a colorimetric method of measurement naturally suggests itself. The usual preliminary experiments were performed in order to learn the maximum amounts that could be measured in this way, the observational errors involved and the effect of temperature changes on the depth of color of the uranium solution. The results are embodied in the procedure and notes below.

Procedure for Colorimetric Measurement.—The precipitation is made in the manner given under the gravimetric method except that the volume of sodium solution should be only one or two cubic centimeters. The precipitate is collected in an unweighed Gooch crucible and washed with four successive portions of 95% alcohol. Air is then drawn through the crucible for five minutes to remove most of the alcohol, after which the precipitate is dissolved through the crucible into a colorimeter tube with warm water (60 to 70°), using it in 2- to 3-cc. portions. The solution is then cooled to room temperature and diluted to some definite volume,

---

[8] It is worth noting that the very large amount of calcium in this solution did not interfere with the precipitation.

between 15 and 25 cc., depending upon the volume of water used in dissolving the precipitate. The depth of color of this solution is next compared with that of a standard solution that has been prepared in the same way.

About 5 mg. of sodium is the maximum amount that can be determined colorimetrically because the amount of uranium compound associated with more than this gives too deep a yellow color for satisfactory comparison. The wash alcohol must be removed in order to avoid cloudy solutions. Good results are obtained only if a colorimeter is employed. Color-comparison tubes alone are not so satisfactory.

It is very important that the solution under analysis and the standard solution be at the same temperature, since the depth of color is strongly affected by the temperature.

The best results are obtained when the solutions show a fairly deep straw color in the colorimeter. At least five readings should be taken with each pair of tubes and the results averaged.

A standard solution of approximately the same concentration as the one under examination should be used. These standard solutions should be prepared by precipitating the sodium from measured portions of standard sodium chloride solution. A convenient strength is 2.542 g. of sodium chloride per liter. One cubic centimeter of this solution contains 1 mg. of sodium.

A peculiar advantage of the colorimetric procedure is that suspended matter need not be removed from the original sodium salt solution. It will be retained in the crucible when the precipitate is dissolved through.

TABLE VIII

EXPERIMENTS ON THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF SODIUM

Sodium present in standards, g.	Depths of standard solns., mm.	Depths of sample solns., mm.	Sodium in sample, g.	Sodium found, g.	Diff. or errors, g.
0.0005	29	25	0.0005	0.0006	+0.0001
	24	22		.0005	.0000
	23	26		.0004	−.0001
.0010	19	43	.0005	.0004	−.0001
	16	38		.0004	−.0001
	20	42		.0005	.0000
.0020	28	22	.0025	.0025	.0000
	25	20		.0025	.0000
	37	31		.0024	−.0001
.0030	26	30	.0025	.0026	+.0001
	30	37		.0024	−.0001
	23	29		.0024	−.0001
.0040	35	30	.0050	.0046	−.0004
	42	35		.0048	−.0002
	28	24		.0047	−.0003
.0060	44	55	.0050	.0048	−.0002
	42	50		.0050	.0000
	36	41		.0052	+.0002

Some typical results obtained by the colorimetric method are given in Table VIII.

The results of Table VIII are seen to be entirely satisfactory except in the instance in which an attempt was made to compare the depths of color of a tube containing 5 mg. of sodium with a standard tube containing 4 mg. More experience with the method will undoubtedly remove such discrepancies.

Summary

1. A method for the direct determination of sodium by precipitating it as magnesium sodium uranyl acetate has been presented.
2. Both gravimetric and colorimetric measurements have been used.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

EMULSIONS: STABILITY, AREA PER MOLECULE IN THE INTERFACIAL FILM, DISTRIBUTION OF SIZES AND THE ORIENTED WEDGE THEORY[1]

BY WILLIAM D. HARKINS AND NORVIL BEEMAN

RECEIVED JANUARY 7, 1929 PUBLISHED JUNE 5, 1929

1. Introduction

When this work was begun no accurate determination had been made of the distribution of sizes of the droplets in emulsions. If such determinations could be made they would give a basis for a decision with respect to three of the most important fundamental problems of this branch of colloid science. These are: (1) the number of molecules of the emulsifying agent per unit area of the oil–water interface, (2) the stability of emulsions and the effect of aging and (3) the oriented wedge theory of emulsions.

While the requirements of the last two problems might be met by large-scale methods, the demands of the first problem seemed to necessitate the use of a fine-scale, or microscopic method, since with large-scale methods there is considerable uncertainty in the theory which is used to translate the scattering of light or the speed of sedimentation into the sizes of the drop?.

2. Experimental Methods

1. Apparatus

1. Microscopic Equipment.—An image of the highly diluted emulsion was projected on a screen by the use of a microscope fitted with a 61x, 3-mm. apochromatic oil immersion objective, 1.40 N.A.; an aplanatic condenser 12-mm., 1.40 N.A.; and a 25x, compensating ocular.

---

[1] A preliminary version of this article was received August 31, 1925.

2. The Cell.—An important part of the equipment was the microscope slide, which was made of thin glass and contained a cell of 4-mm. diameter with a depth of 0.10 mm. which was covered by a thin cover glass. The bottom of this cell was ruled in squares and it was surrounded by a circular depression 0.5 mm. deep and 3 mm. wide. Two small grooves leading from this depression allow any excess of solution to flow away when the cover glass is put in place, The use of a drop of the emulsion suspended from the bottom of a cover glass gives poor results since the surface forces cause a considerable segregation of the droplets according to their sizes.

2. Preparation of Emulsions

1. Materials. Oils.—The octane was the synthetic substance obtained from the Eastman Laboratories, Rochester, N. Y. The "Stanolax" was a heavy paraffin oil sold by the Standard Oil Company of Indiana. Kahlbaum's benzol, thiophene-free, was also used.

Water.—The water used for making the emulsions and for cleaning the slide and cover glasses was distilled water examined periodically to assure freedom from suspended particles of microscopic size.

Soaps.—The oleate soaps were made from oleic acid, U. S. P., after extensive purification by both the lead salt and barium salt treatments[2] and finally by a vacuum distillation.

The sodium and potassium oleates were made by dissolving the solid alkali metal in absolute alcohol, filtering to remove any carbonate, adding oleic acid and evaporating to dryness. The residue was then dissolved in absolute alcohol and refluxed for a half hour. (The amount of oleic acid was arbitrarily determined according to the method used by Laing[3] in which the acid was added until the alcoholic solution after dilution with a recently boiled mixture of alcohol and water (3:1) was found by repeated tests to give a neutral reaction with neutral alcoholic solution of phenolphthalein.) The hot solution was now filtered through a hot-water funnel and the soap allowed to crystallize out. It was then drained, washed with absolute alcohol and ether and dried.

For the cesium oleate, cesium nitrate was converted into cesium carbonate by fusion with oxalic acid. An excess of the carbonate was dissolved in a small volume of water, the oleic acid dissolved in 95% alcohol, the two solutions were mixed and evaporated to dryness. The residue was dissolved in absolute alcohol, the exact amount of oleic acid being determined as before. The solution was filtered and again evaporated to dryness. After redissolving in absolute alcohol the procedure was the same as for sodium and potassium oleates. Cesium oleate is a fairly "soft" soap and does not crystallize out readily even in the cold.

The stearates and other soaps were made in much the same manner. Kahlbaum's best stearic acid was used for the stearate soaps. The chaulmoogric acid was obtained from Professor B. H. Nicolet and was a sample sent to this Laboratory for research purposes in connection with the chaulmoogra oil treatment for leprosy. The elaidic acid was purified by Mr. T. C. Poulter in this Laboratory.

Aluminum and magnesium oleates were made by the precipitation of these oleates from sodium oleate solutions followed by purification by recrystallization from absolute alcohol.

Through the kindness of Professor J. H. Hildebrand samples of the sodium and cesium stearates formerly used in work with emulsions at the University of California were also tried.

---

[2] Vanino, "Praparative Chemie," Vol. II, p. 120; Lewkowitsch, "Chemical Technology," 1909, Vol. I, p. 140.

[3] Mary E. Laing, J. *Chem. Soc.*, 119, 1669 (1921).

2. Procedure.—The general method followed for oil in water emulsions was to make a fresh soap solution of the concentration desired, add an equal quantity of oil and then beat or stir to form the emulsion. The beating was done by a motor-driven egg beater, the stirring by an Arnold drink mixer. For the former **7** to **10** cc. of soap solution and an equal volume of oil were most convenient; for the latter *5* cc. or more of each phase was put in a large flat-bottomed test-tube. The time of beating and stirring was varied according to purpose but more commonly emulsions were given twenty minutes' beating by the egg beater or, if stirring was the method, ten minutes' stirring with the drink mixer. **A** Briggs' homogenizer was used, except in special cases, and the emulsion after beating or stirring was drawn through about five times by suction. The homogenizer was especially of service in removing air bubbles formed during beating. *Unstable emulsions were easily broken by homogenization* and this treatment was omitted in such cases, the air bubbles if found present being removed by subjecting the emulsion to a vacuum treatment.

There seems to be ***a*** definite relation between foaming and efficiency of emulsification. This applies particularly to emulsification with dilute soaps. It was noticed that emulsions which did not foam up during the beating—and this was rather characteristic of emulsions made with very dilute soaps—separated more readily than those which did foam, though some very stable emulsions were made which did not foam. It was a common practice in such cases to beat the soap solution to a foam and then add the oil in a thin stream or in portions whiie beating.

3. Method of **Sampling.—The** emulsion—cream, aqueous phase and all—was mixed by running it back and forth from end to end of the test-tube which contained it. Care was taken to prevent formation of foam during this mixing. From this thoroughly mixed emulsion **3** or 4 drops were pipetted out and diluted in microscopically clear distilled water. The degree of dilution depended upon the emulsion, varying from 1 drop in **300** cc. of water in some octane emulsions, in which the particles were very small and more numerous, to 8 or 9 drops in **300** cc. of water for some Stanolax emulsions, in which the drops were much larger and less numerous. Immediately after dilution the sample was pipetted out, placed upon the slide and covered with a cover glass. Oil contacts between condenser and slide and between cover glass and objective were made with Stanolax since it was more easily cleaned off and does not harden after exposure to the air as cedar oil does.

4. Cleaning the Slide and Cover Glass.—The slide and cover glass must be thoroughly clean if good results are to be obtained. Sticking of drops to the cover glass was avoided entirely by the following method. The slide and cover glass were washed in soap solution. Just before use the cover glass and slide were removed from the soap solution and rinsed well with clear, distilled water. This rinse water was shaken off and the sample placed between the *wet* slide and a *wet* cover glass. For water in oil emulsions the slide and cover glass were cleaned as before, dried with alcohol and ether, and then dipped into some of the same oil as that of the continuous phase of the emulsion to be examined.

5. Measuring the Drops.—The sample was diluted so that there were about **10** or **12** drops in the field at one time. Measurements were taken upon every drop from the bottom of the cell to the cover glass in a strip across the cell from one edge to the other. This strip was definitely determined by lines drawn in a horizontal direction across the scale on the screen.

The smallest drops up to **1** micron in diameter were recorded and plotted as ***0.5*** micron, from 1 to ***2*** as 1.5 micron, from ***2*** to ***3*** as ***2.5*** microns, etc.

Exact measurements upon moving spheres of varied sizes are difficult because the sizes seem to change with the change of focus of the microscope, intensity of illumination, direction of the beam of light, condition of the eyes with respect to presence or absence of fatigue, etc. For this reason a finer scale was not used in the classification.

3. Effects of Various Monovalent Cations on the Distribution of Sizes

The distribution of sizes (diameters) of the oil droplets in emulsions produced by oleate soaps is found to be exactly the same, within the experimental limits of accuracy, for any of the three univalent cations, lithium, sodium and cesium. This is shown to be true in emulsions of a very viscous paraffin oil (Fig. 1) and in those in which the oil is extremely fluid, such as octane or hexane (Figs. 2 and 3). According to the method used in plotting, each point gives the number of drops per 100 counted of the size designated. Thus the maximum number found in these figures occurs at 1.5 microns, and for emulsions of Stanolax the number for this size is **30.** That is, in the Stanolax emulsion 30% of the droplets have diameters between 1 and 2 microns.

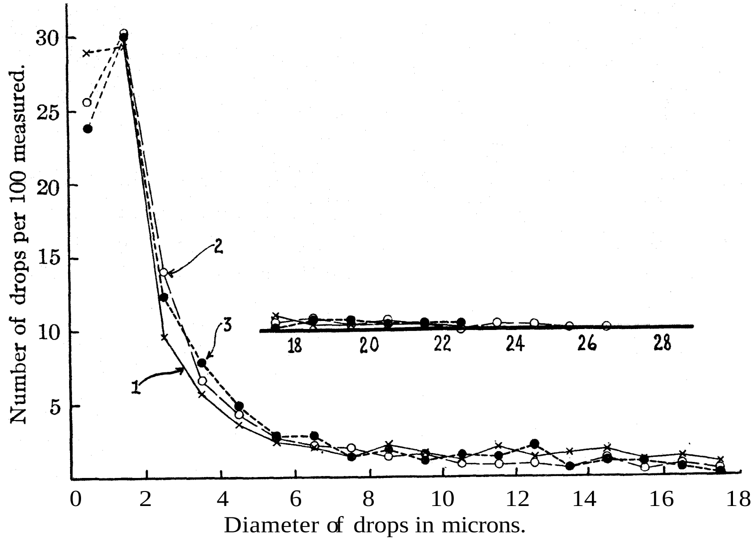


Fig. 1.—Stanolax emulsions beaten by egg beater. 1, $M/10$ sodium oleate, ×—×—×; 2, $M/10$ potassium oleate, ○--○--○; 3, $M/10$ cesium oleate, ●···●···●.

A forced variation from this general procedure occurs for the points at 0.5 micron, which represent the number of droplets between 1μ as the upper limit and about 0.1μ (the limit of visibility) as the lower limit. Obviously if ultramicroscopic droplets were counted, the number represented at 0.5μ would be greater, but it is improbable that the distribution of area of the interface is greatly affected by this omission.

The results described above have a bearing upon the extent of application of the oriented wedge theory. Langmuir considered that the form of colloidal particles of oleic acid is determined by the *adsorption of hydroxyl* groups: "If a film of closely packed oleic molecules covers the surface to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downward in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consists of COOH groups together with adsorbed OH, while the interior consists of the long hydrocarbon chains.

"The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of the arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed."[4]

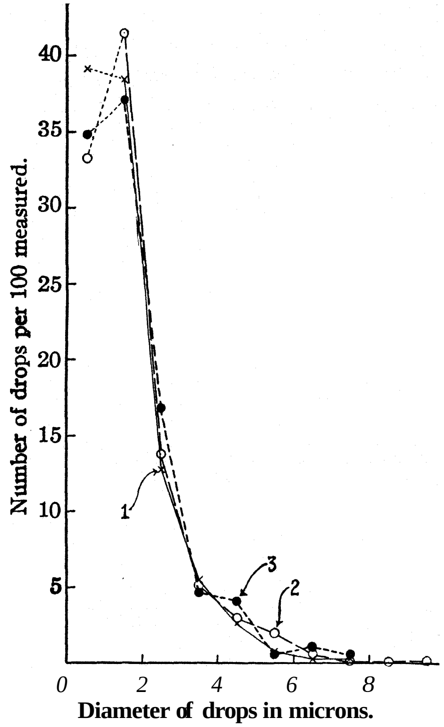


Fig. 2.—Octane emulsions beaten by egg beater: 1, $M/10$ sodium oleate, X—X—X; 2, $M/10$ cesium oleate, O—O—O; 3, $M/10$ cesium oleate, ●—●—●. Curves 2 and 3 show the effect of aging an emulsion produced by 0.1 molal cesium oleate. Curve 2 was obtained on the day of preparation and Curve 3 one month later.

The idea that the number of hydrocarbon groups associated with one ion of a metal determines whether the emulsion shall be one of oil in water (univalent cation) or of water in oil (polyvalent cation) was advanced by Harkins, Davies and Clark,[5] as shown in the following quotation.

"The molecules in the surfaces of liquids seem to be oriented, and in such a way that the least active or least polar groups are oriented toward the vapor phase. The general law for surfaces seem to be as follows: *if we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase, and at any surface or interface the change which occurs is such as to make the*

---

[4] Langmuir, *Chem. Met. Eng.*, 15, 468 (1916); THIS JOURNAL, **39**, **1848 (1917)**.

[5] **Harkins, Brown and Davies,** *ibid.*, 39, 354–364 (1917); Harkins, **Davies and Clark,** *ibid.*, 39, 541–596 (1917); **and later papers.**

transition to the adjacent phase less abrupt. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a "double electrical layer" at the surfaces of liquids and also of solids.

"This law if applied to special cases indicates for a few pure liquids the following orientation: In water the hydrogen atoms turn toward the vapor phase and the oxygen atoms toward the liquid. With organic paraffin derivatives the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the interior of the liquid.

"If any of these organic compounds are dissolved in water, their orientation in the water surface is the same as that just given, with the active groups inward.

"At interfaces between two pure liquids the molecules turn so that their *like* parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid A are as much like A as possible and the ends toward B are as much like B as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid and the polar group toward the water. . . . .

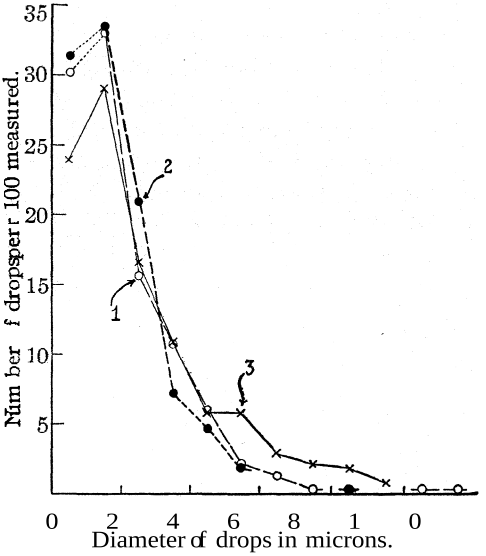


Fig. 3.—Octane emulsions stirred by drink mixer: 1, $M/200$ sodium stearate, O—O—O; 2, $M/200$ cesium stearate, ●—●—●. Stanolax emulsion beaten by egg beater and inverted: 3, $M/10$ sodium oleate, X—X—X, after inversion with aluminum nitrate. Curve 3 represents a water in oil emulsion.

"When Newman, working with Bancroft in 1914, found that while sodium oleate in solution will give emulsions of benzene in water, and the oleate salts of a metal with a valence higher than one will give emulsions of water in benzene, we were working experimentally in this Laboratory on the adsorption of these long hydrocarbon chains. Now while Bancroft seemed to think that this work indicated that the liquid with the higher surface tension forms the inner phase, it seemed to us that the only apparent relation was that to the *number of oleate radicals* in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore, it quite possibly may be the orientation and the form of the molecules together with adsorbed ions in the interface between the dispersoid particles (or small drops), and the dispersion medium which determine the surface energy relations; and, therefore, the size of the drop at which it becomes stable. In other words, this idea is that the drop would be stable whenever the molecules, together with adsorbed ions, etc., in the interface, fit the curvature of the drop. The molecules in the curved surface would not need to be all of the same kind. If the molecules do not fit in the curved surface, the drop will not be perfectly stable and will either decrease or increase in size if given time."

This "oriented wedge theory" of emulsions was, seemingly, given strong support by the experimental results of Finkle, Draper and Hildebrand,[6] who determined the distribution of the number of drops according to their diameters in solutions of sodium, potassium and cesium palmitate, which were used as emulsifying agents. Thus they kept the negative ion constant but varied the positive ion. The latter is, presumably, turned toward the outside of the drop, that is, toward the aqueous phase. Now it is known that the *atoms,* sodium, potassium and cesium, increase in diameter in the order given, so if the atoms are effective in the sense of the wedge theory, the outer part of the wedge increases in size in the same order and this would increase the curvature in just this order. Thus the droplets of oil should decrease in diameter as the emulsifying agent is changed from sodium to potassium and cesium oleate, and this is just what was found in the experiments of Finkle, Draper and Hildebrand. Preliminary results obtained by Harkins and Keith[7] also seemed to agree entirely with theirs, but later, upon the more careful elimination of all factors which might cause some type of segregation and the use of a more suitable optical system, the result presented above was obtained.

However, there is another more proper point of view according to which *the oriented wedge theory does not indicate any such decrease in size of the droplets in the change from sodium to cesium.* The negative oleate ions are adsorbed at the oil–water interface with the hydrocarbon radical toward the oil and the –COO– group toward the water. The Na^+ or Cs^+ ions are held to these by electrostatic attractions alone, so the alkali ions form a diffuse but extremely thin positively charged layer, in which the distribution may follow the Boltzmann e-theorem. A part of the soap in the film is present as oleic acid formed by hydrolysis. From this point of view it seems improbable that the sizes of the atoms will produce any marked influence upon the sizes of the droplets. It is known too that the smaller the alkali atom, the more highly hydrated is its ion.

---

[6] Finkle, Draper and Hildebrand, THIS JOURNAL, 45, 2780 **(1923).**

[7] Harkins and Keith, *Science,* 59, 463–467 *(1924).*

When, on the other hand, the ion of the metal is bi- or tri-valent, the electrostatic relations are such that in general two $RCOO^-$ ions are held by only one M^{++} ion. Such conditions are favorable to the expansion of that side of the film which is turned toward the oil by the spreading of the hydrocarbon chains. Thus the addition of aluminum nitrate to an emulsion produced by sodium oleate inverts the emulsion and changes it to the water in oil type.

It was found by Harkins and Keith that when a drop of the emulsion is suspended from a cover glass, there is a segregation of the microscopic droplets in the emulsion according to their sizes. This makes it extremely difficult to obtain a correct determination of the distribution of sizes, and is undoubtedly the cause of the discrepancy between the earlier work and that presented here.

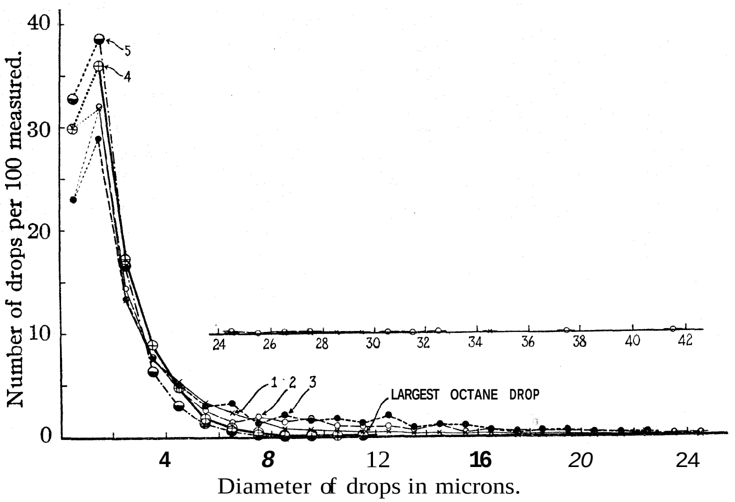


Fig. 4.—Distribution of diameters in emulsions of octane and Stanolax stabilized by sodium, potassium and cesium oleates. Stanolax emulsions: 1, sodium soaps, ×—×—×; 2, potassium soaps, O--O--O; 3, cesium soaps, ●--●--●. Octane emulsions: 4, sodium soaps, ⊕—⊕—⊕; 5, cesium soaps, ⊖-·-⊖-·-⊖.

4. Influence of the Viscosity of the Oil

Although the viscous paraffin oil (Stanolax) had a viscosity more than 150 times that of the octane, it is remarkable that with either oil the greatest number of droplets occurs between 1 and 2μ, that is, the peak in the distribution according to diameters occurs at the same place for either oil. The marked difference illustrated by Fig 4 is that of the larger drops. Thus the largest of the 5668 octane droplets represented by this figure had a diameter of about 10.5μ, while the diameters of those of Stanolax were as great as 41.5μ, or nearly four times as great. The effect of the viscosity of the oil is exhibited by Tables IA and IB, and by Figs. 4 and 5. Fig. 5 illustrates a Stanolax emulsion produced by 0.1 *M* sodium oleate.

TABLE IA (SEE FIG. 6)

COMBINED OCTANE EMULSIONS MADE BY DRINK MIXER BUT DISREGARDING THE KIND OF SOAP (0.1 M AQUEOUS SOLUTIONS)

Mean diam.	Actual no. of drops	%	No. as taken from smoothed curve	1a % as taken from smoothed curve	2a Sq. cm. of area per cc. of oil × 10^{-3}	3a Volume per cc. of oil, cc.
0.5	806	33.31	806	33.306	0.791	0.0099
1.5	918	37.93	918	37.934	3.605	.0901
2.5	408	16.86	408	16.859	4.452	.1855
3.5	171	7.07	171	7.066	3.656	.2133
4.5	73	3.02	73	3.016	2.580	.1935
5.5	29	1.20	29	1.198	1.531	.1404
6.5	10	0.41	10	0.413	0.737	.0799
7.5	2	.08	2.97	.123	.292	.0364
8.5	1	.04	1.08	.045	.136	.0193
9.5	0	.00	0.41	.017	.065	.0102
10.5	1	.04	.31	.013	.060	.0104
11.5	1	.04	.16	.007	.037	.0071
12.5	0	.00	.07	.003	.019	.0040
	2420	100.00	2420.00	100.000	17.961	1.0000

TABLE IB

COMBINED STANOLAX EMULSIONS MADE BY DRINK MIXER BUT DISREGARDING THE KIND OF SOAP (0.1 M AQUEOUS SOLUTIONS)

Mean diam.	Actual no. of drops	%	No. as taken from smoothed curve	1b % as taken from smoothed curve	2b Sq. cm. of area per cc. of oil × 10^{-3}	3b Volume per cc. of oil, cc.
0.5	1283	31.923	1283	31.920	0.245	0.0031
1.5	1266	31.500	1266	31.500	0.969	.0242
2.5	538	13.386	538	13.380	1.144	.0476
3.5	314	7.813	337.6	8.400	1.407	.0821
4.5	242	6.021	227.5	5.660	1.567	.1175
5.5	165	4.105	154.7,	3.850	1.592	.1459
6.5	98	2.438	97.6	2.430	1.403	.1520
7.5	68	1.692	56.3	1.400	1.077	.1347
8.5	18	0.448	31.7	0.790	0.779	.1104
9.5	16	.398	15.8	.395	.485	.0768
10.5	4	.100	4.9	.123	.184	.0322
11.5	1	.025	2.4	.062	.108	.0207
12.5	4	.100	1.4	.035	.074	.0165
13.5	0	.000	0.9	.023	.056	.0125
14.5	0	.000	.6	.014	.043	.0104
15.5	1	.025	.3	.009	.025	.0063
16.5	1	.025	.2	.005	.019	.0051
17.5	0	.000	.1	.003	.010	.0030
	4019	99.999	4019.0	99.999	11.187	1.0000

The most regular results are given by emulsions prepared by the drink mixer (Fig. 6).

5. Influence of the Concentration of the Soap

No appreciable influence of change in soap concentration upon the distribution of diameters in freshly *made* emulsions was discovered. Isolated cases here and there might suggest such a relation but on the whole no positive conclusions could be drawn. With emulsions permanent enough to measure, the difference in soap concentration produced little or no detectable effect. On the other hand, as the emulsions aged, a decided effect was observed in the cases of dilute emulsions. This effect is discussed in the next paragraph.

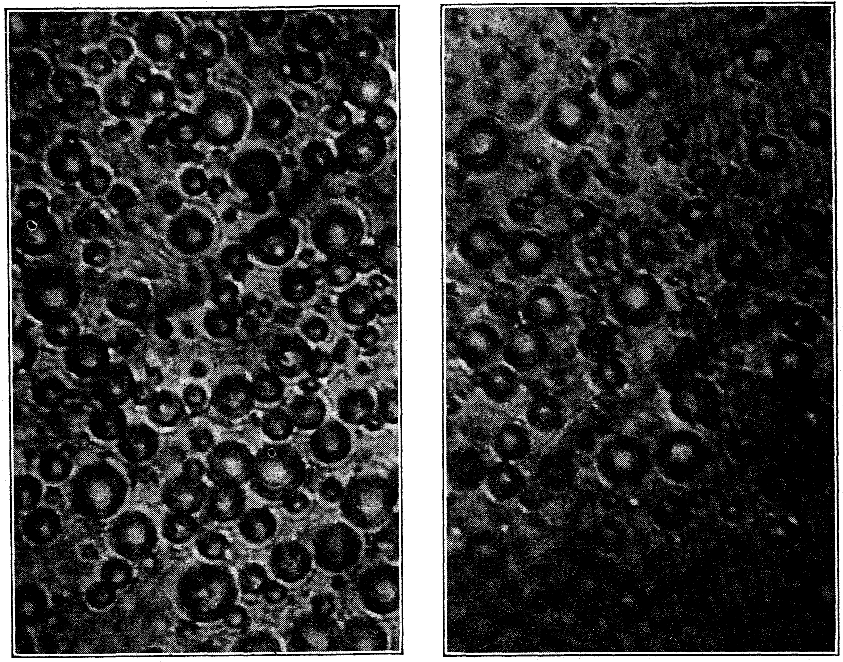


Fig. 5.—Stanolax emulsion (X 1000). Diluted 100 times. The emulsifying agent was 0.1 M sodium oleate. (Taken by R. S. Dean.)

6. Stability: Effect of Aging

The stability of certain emulsions has been ascertained by a determination of the variation of the distribution of sizes (diameters, areas and volumes) with the time. It is evident that this gives much information concerning the stability not indicated at all by the older method of merely observing the gross features of the emulsion such as the separation of oil in bulk (Tables II and III).

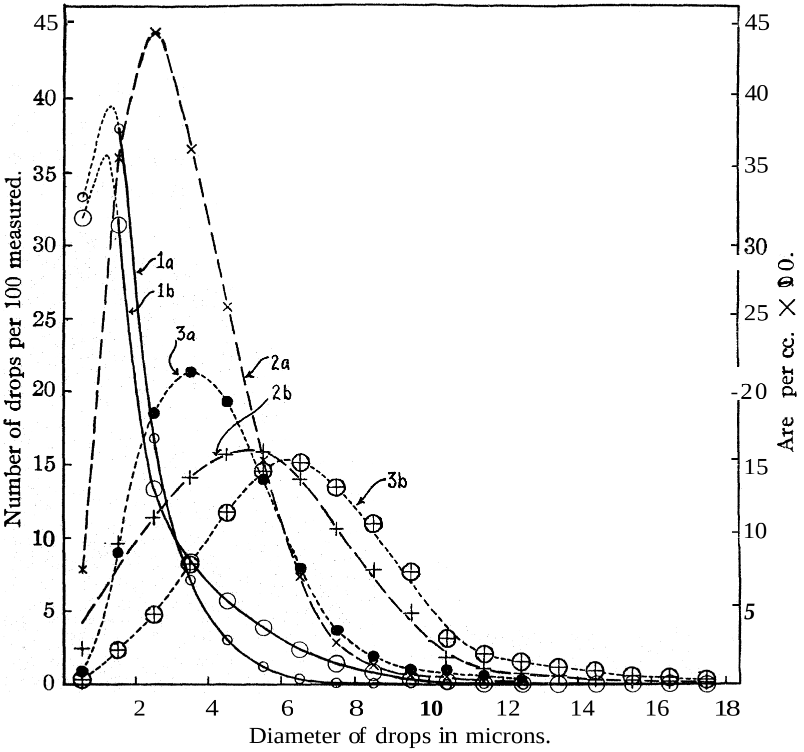


Fig. 6.—This figure represents measurements on about 2500 droplets of octane and 4000 of Stanolax, numbers so large as to give smooth curves. Comparison of octane and Stanolax emulsions made by drink mixer. Diameter distribution: 1a, octane, o—o—o; 1b, Stanolax, O—O—O. Area distribution (area/cc. X 10): 2a, octane, X—X—X; 2b, Stanolax, +—+—+. Volume distribution (vol. X 100): 3a, octane, ●--●--●; 3b, Stanolax, ⊕--⊕--⊕.

TABLE II (SEE FIG. 8)

CHANGES IN DISTRIBUTION OF DIAMETERS WITH AGING

$M/200$ NaOl and octane stirred by the drink mixer

	1a First day		1b Third day		1c Seventh day	
Mean diam.	No. of drops	%	No. of drops	%	No. of drops	%
0.5	100	30.9	15	4.7	8	4.3
1.5	139	42.9	71	22.4	19	10.1
2.5	68	21.0	103	32.5	23	12.2
3.5	15	4.6	72	22.7	36	19.2
4.5	2	0.6	36	11.4	40	21.3
5.5			12	3.8	29	15.4
6.5			5	1.6	23	12 2
7.5			2	0.6	7	3.7
8.5			1	0.3	2	1.1
9.5					1	0.5
	324	100.0	317	100.0	188	100.0

Table II (Concluded)

$M/200$ CsOl and octane stirred by the drink mixer

Mean diam.	2a First day No of drops	%	2b Third day No. of drops	%	2c Seventh day No of drops	%
0.5	142	34.9	20	6.4	7	3.6
1.5	183	45.0	87	27.8	16	8.2
2.5	59	14.5	80	25.5	23	11.8
3.5	19	4.7	62	19.8	38	19.5
4.5	3	.7	40	12.8	40	20.5
5.6	1	.2	14	4.5	29	14.9
6.5			6	1.9	16	8.2
7.5			3	1.0	14	7.2
8 5			0	0.0	8	4.1
9.5			1	0.3	1	0.5
10.5					1	.5
11.5					0	.0
12.5					1	.5
13.5					1	.5
	407	100.0	313	100.0	195	100.0

Table III (See Fig. 9)

CHANGES IN AREA AND VOLUME WITH AGING

$M/200$ NaOl and octane (same emulsion as given in Table II)

	Changes in area, sq. cm. of area per cc. of oil X 10^{-3}		Changes in volume, cc. of volume per cc. of oil	
Mean diam. in microns	1a First day	1b Third day	2a First day	2b Third day
0.5	1.407	0.039	0.0176	0.0005
1.5	7.822	0.735	.1955	.0184
2.5	10.629	2.960	.4429	.1233
3.5	4.595	4.055	.2681	.2365
4.5	1.013	3.352	.0759	.2514
5.5		1.669		.1530
6 5		0.971		.1052
7.5		.517		.0646
8.5		.332		.0471
	25.466	14.630	1,0000	1.0000

$M/200$ CsOl and octane (same emulsion as given in Table II)

	Changes in area, sq. cm. of area per cc. of oil X 10^{-3}		Changes in volume, cc. of volume per cc. of oil	
Mean diam. in microns	1a First day	1b Third day	2a First day	2b Third day
0.5	1 679	0.048	0.0210	0.0006
1.5	8 657	0.842	.2164	.0210
2.5	7.753	2.150	.3230	.0896
3.5	4.894	3.265	.2855	.1905
4.5	1.277	3.483	.0958	.2612
5.5	0.0636	1.821	.0583	.1669
6.5		1.090		.1181
7.5		0.726		.0907
8.5		.000		.0000
9.5		.388		.0614
	24.896	13.813	1.0000	1.0000

The more concentrated soap solutions seem to form emulsions which are very stable even over long periods of time. Emulsions made with 0.1 *M* soap solutions and with greater concentrations, where the soap is soluble enough to remain in solution, were not observed to change appreciably in the course of a year. One possible exception was 0.1 M potassium chaulmoograte and Stanolax (see under "Influence of Different Hydrocarbon Chains"). Curves 2 and **3,** Fig. 2, are fairly representative of the effect of aging emulsions produced by 0.1 M soaps. Curve 2 is for a 0.1 M cesium oleate and octane emulsion; Curve **3** is for the same emulsion more than a month later.

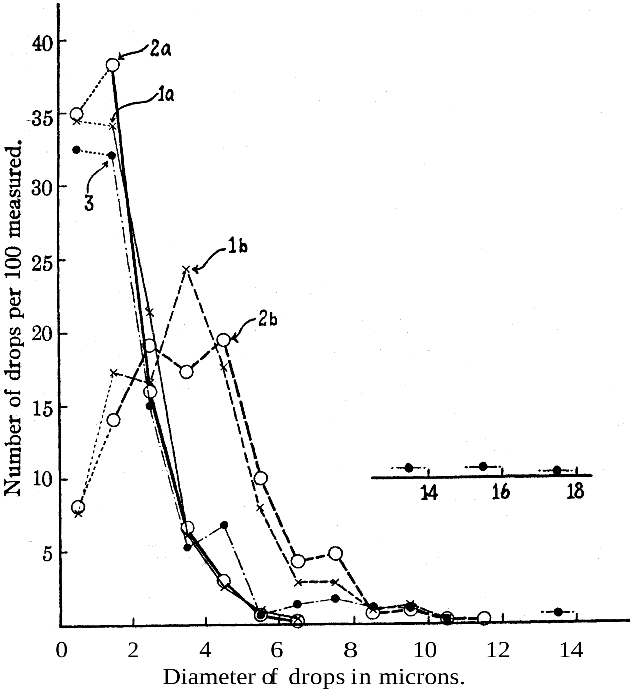


Fig. 7.—Changes in diameter distribution with aging. *M*/100 sodium oleate and octane (drink mixer): 1a, measured on first day; 1b, measured on tenth day. *M*/100 cesium oleate and octane (drink mixer): 2a, measured on first day; 2b, measured on tenth day. *M*/100 sodium oleate and octane (egg beater and different soap): 3, measured fifteen and one-half months later.

At the other extreme, emulsions' produced by very dilute soaps were found to change rapidly. Thus 0.0005 M, 0.0008 M and 0.008 M soaps gave unstable emulsions which showed signs of breaking within a few hours after making. The most dilute soap which produced an emulsion (Table IV) stable long enough to measure had a concentration of 0.0008 M.

(A measurement required from one to two hours.) Soaps of a concentration of 0.005 M gave emulsions which broke markedly within a few days in some cases, while in others they were stable to all appearances except to microscopic observation. In every case, whether they broke ultimately or not, the microscope showed unmistakable changes in all of the 0.005 *M* emulsions studied. Figs. 7 and 8 exhibit the changes produced by aging in the diameter distribution and Figs. 9 and 10 in the area and volume distributions for emulsions of octane made with 0.01 M and 0.005 M solutions of cesium and sodium oleates. An actual shift in maxima and a relative increase in the number of large drops accompany aging of all the emulsions made with 0.005 M sodium and cesium oleates.

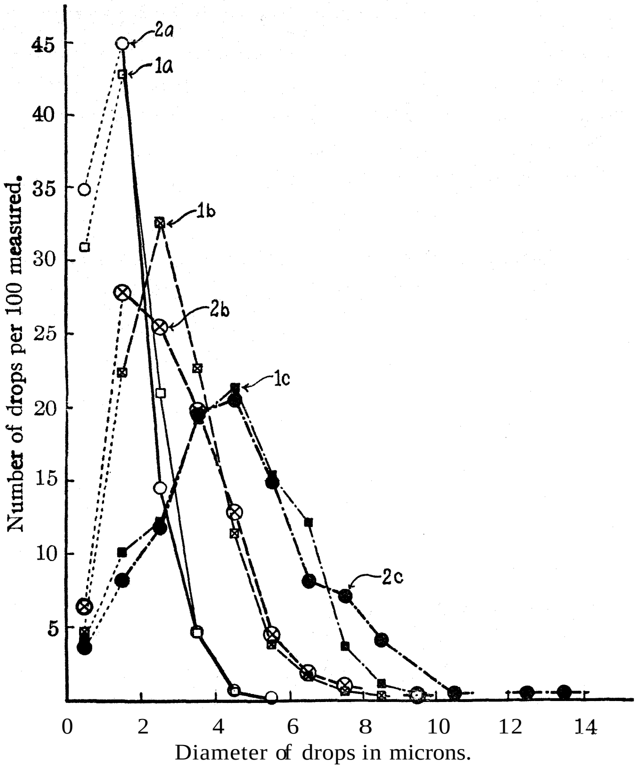


Fig. 8.—Changes in diameter distribution with aging. *M*/200 sodium oleate and octane (drink mixer): 1a, measured on first day, 1b, measured on third day; 1c, measured on seventh day. *M*/200 cesium oleate and octane (drink mixer): 2a, measured on first day; 2b, measured on third day; 2c, measured on seventh day.

Thus an emulsion produced from equal quantities of octane and a 0.005 M aqueous solution of *sodium oleate* gave an area of 25,466 sq. cm. per cc. of oil immediately after it was prepared, and 14,630 sq. cm. on the third day later. It is remarkable how closely these values were duplicated by an emulsion prepared with the same concentration of cesium oleate: 25,000 sq. cm. at first, and 13,813 sq. cm. on the third day.

Emulsions produced by 0.01 *M* soaps were much more stable (Fig. 7), and changed less in ten days than those with 0.005 M soap in seven days.

7. Influence of Different Methods of Preparation

It was found that twenty minutes' stirring with a motor-driven egg beater, or ten with a high-speed drink mixer gave the same distribution of sizes as double these periods. The drink mixer gave fewer large drops, but the remarkable feature was that either the beater or the mixer, or shaking by hand, gave the same position for the peak in the curve.

TABLE IV

RELATION OF AREA AT INTERFACE TO VOLUME OF A VERY DILUTE EMULSION

M/1200 NaOl and Stanolax stirred by drink mixer

Mean diam.	Actual no. of drops	%	Sq. cm. of area $\times 10^5$	Sq. cm. of area per cc. of oil $\times 10^{-5}$	Cc. of volume $\times 10^{10}$	Cc. of volume per cc. of oil
0.5	338	41.4	0.597	0.469	0.747	0.006
1.5	331	40.5	2.340	1.836	5.849	.046
2.5	83	10.2	1.630	1.279	6.790	.053
3.5	28	3.4	1.077	0.845	6.286	.049
4.5	9	1.1	0.573	.449	4.294	.034
5.5	10	1.2	0.950	.746	8.711	.068
6.5	8	1.0	1.062	.833	11.504	.090
7.5	2	0.2	.353	.277	4.417	.035
8.5	0	.0	.000	.000	0.000	.000
9.5	3	.4	.851	.667	13.468	.106
10.5	2	.2	.693	.544	12.122	.095
11.5	0	.0	.000	.000	0.000	.000
12.5	1	.1	.491	.385	10.227	.080
13.5	0	.0	.000	.000	0.000	.000
14.5	0	.0	.000	.000	0.000	.000
15.5	1	.1	.755	.592	19.498	.153
16.5	1	.1	.855	.671	23.521	.185
	817	99.9	12.227	9.593	127.434	1.000

8. Influence of the Addition of a Second Substance to the Soap

Surface tension work in this Laboratory has shown the marked effects of the addition of a substance like sodium hydroxide or oleic acid to a solution of sodium oleate. In contrast, the results obtained in this investigation when sodium hydroxide or oleic acid was added to the sodium oleate used as an emulsifying agent showed only slight effects upon the distribution curve. Various concentrations of sodium hydroxide were added to a 0.1 *M* sodium oleate solution and emulsions made by the use of each of these for the aqueous phase. Measurements were made on each emulsion but no markedly great effect was noticed until the concentration of the base had reached 1 M. At this concentration the diameter distribution was altered by a decrease in the number of large drops and an increase in the number of small drops. A similar change was obtained with the addition of 0.1 M oleic acid. The emulsion seemed to be more sensitive to the addition of oleic acid than of sodium hydroxide, though not sensitive to low concentrations of either.

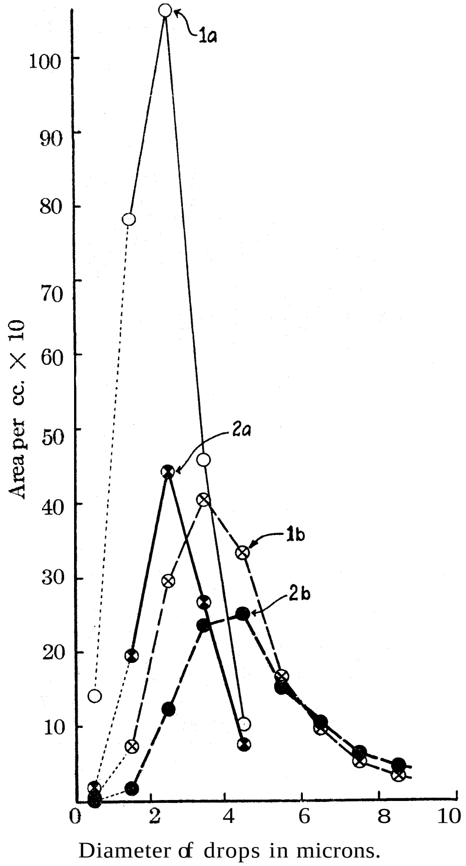


Fig. 9.—Changes with aging. $M/200$ sodium oleate and octane (same as in Fig. 8). Changes in area: 1a, measured on first day; 1b, measured on third day. Changes in volume: 2a, measured on first day; 2b, measured on third day.

9. Influence of Different Hydrocarbon Chains

Sodium stearate, elaidate and cerotate were used as stabilizing agents with the result that the same general distribution of sizes was obtained. Some other means of measuring particles smaller than one micron in diameter might indicate differences in the distribution of diameters of the smaller drops. In the case of the cerotate the emulsion which formed was very stiff and jelly-like and measurement was so difficult it could only be carried out roughly.

With 0.1 M potassium chaulmoograte and Stanolax, beaten by the egg beater, a surprisingly large number of the smaller drops was found. Thus the number of those of a mean diameter of 0.5 micron was almost twice the number of those of a diameter of 1.5 microns. Potassium chaulmoograte was found to be a very soluble soap but the emulsions made with it were not as stable as the emulsions made with potassium oleate. Very shortly after beating, whether the emulsion was run through the homogenizer or not, a thin layer of Stanolax separated out.

10. Water in Oil Emulsions: Influence of Metals Other Than Univalent

Magnesium and aluminum oleates were dissolved in Stanolax and equal volumes of this oil and water were emulsified. They gave water in oil emulsions which when measured were found to give diameter distributions of the same type as those found for oil in water emulsions.

A Stanolax emulsion with 0.1 M sodium oleate made in the usual manner was inverted by the addition of the required quantity of aluminum nitrate. The inversion was carried out while beating. When this emulsion was measured it was found to be of the same general type (Curve **3**, Fig. **3** and Table V). The same procedure was carried out with magnesium nitrate and again an inverted emulsion was the result, but in this case the drops were not spherical but irregular and gave the appearance of being inclosed in solid films. **A** careful set of measurements was impossible but a rough one was made and the usual distribution of sizes was indicated. These water-in-oil emulsions were not very stable and were almost entirely broken after a week or so.

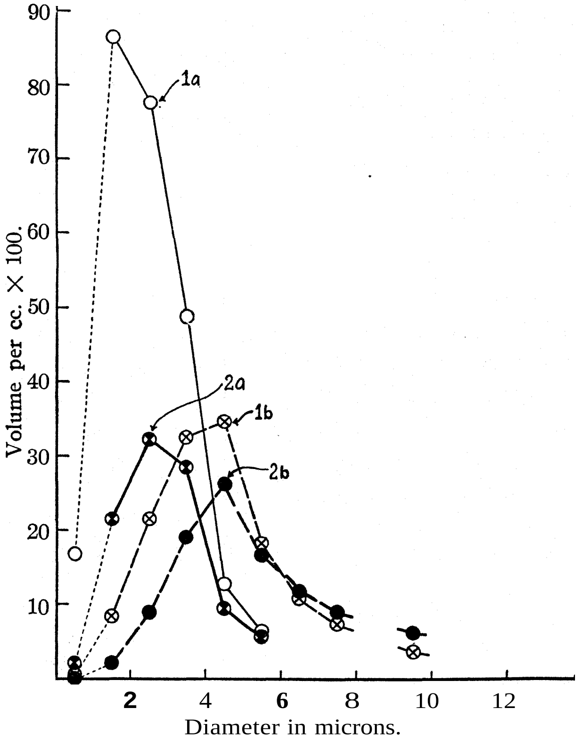


Fig. 10.—Changes with aging. $M/200$ cesium oleate and octane (same as in Fig. 8). Changes in area: 1a, measured on first day; 1b, measured on third day. Changes in volume: 2a, measured on first day; 2b, measured on third day.

A large quantity of sodium oleate dissolved in Stanolax by warming set to a jelly-like consistency upon cooling. To **this** solution of sodium oleate in oil was added water, while beating, and a water-in-oil emulsion was formed which broke within a few hours. This method was used by Harkins and Keith.'

TABLE V

DISTRIBUTION OF DIAMETERS IN A WATER-IN-OIL EMULSION OBTAINED BY INVERTING AN EMULSION OF STANOLAX PRODUCED WITH 0.1 M SODIUM OLEATE BY THE ADDITION OF ALUMINUM NITRATE

Diameter	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	Total
No, of drops	66	SO	46	30	16	16	8	6	5	2	275
Per cent.	24.0	29.0	16.8	10.9	5.8	5.8	2.9	2.2	1.8	0.8	100.0

11. Emulsions Made .without a Stabilizing Agent

It was noticed in the emulsion made with magnesium and aluminum oleates, which were of the water-in-oil type, that the aqueous layers had a very cloudy appearance. When examined under the microscope they were found to contain oil drops, that is, these aqueous layers were dilute oil-in-water emulsions. This led to the examination of both layers of an emulsion formed by stirring together equal volumes of Stanolax and water without using a stabilizing agent. About two hours after stirring samples were taken from each layer. In the oil layer was found a water-in-oil emulsion, and in the water layer an oil-in-water emulsion, but in the latter the concentration of droplets was about ten times greater than in the former. Measurements taken on the drops in these two layers showed diameter–distribution curves of the usual type except that the curves extended distinctly upward from the 1.5 micron to the 0.5 micron points, there being about 5% more drops of 0.5μ than of the 1.5 micron mean diameter in each case.

12. Emulsions of Benzene in Aqueous Soap Solutions

Benzene in water emulsions were made with different soaps. The distribution of diameters was of the usual type, except that more drops were observed between 0 and 1μ in diameter than between 1 and 2μ. As compared with those of Stanolax and octane, emulsions of benzene contained many more small particles.

13. Area at the Interface

Area is of prime importance in a study of colloids because of its relation to the phenomenon of adsorption. For those octane emulsions which are very stable it is seen that the greatest area is furnished by drops of approximately 2.0 to 2.5 microns in diameter[8] (see Curve 2a, Fig. 6). This holds

---

[8] The first point in the area and volume curves is calculated upon the assumption that 0.75 micron is the mean diameter rather than 0.5 micron, though it is made to appear in the graphs as 0.5 micron. That is, it is felt that 0.75 micron rather than 0.5 micron represents more nearly the mean diameter of the very smallest drops visible by means of our optical system.

fairly well for the less stable emulsions also, but only if they are fresh (see Curves 1a, Fig. 9, and 1a, Fig. 10). Stanolax emulsions exhibit a different relation since the diameter which gives the maximum area is about 5 microns, since relatively fewer small drops are formed from the more viscous oil.

As indicated in Figs. 7 and 8 the aging of emulsions stabilized by rather dilute soaps is an important factor in the change of number, area and volume distributions. With a 0.005 M soap the shift of the maximum of the diameter-distribution curve for octane is about **3** microns in six days, or 0.5 micron per day. With 0.01 *M* soap the shift for the same oil, in two cases out of three, was about 2 microns in nine days, or 0.2 micron per day. This may be taken as a measure of the relative stability of these two emulsions. No shift in emulsions made with 0.1 M soaps was discovered, these apparently having more than enough soap to stabilize the interfacial film and, at the same time, enough soap in the aqueous phase to maintain equilibrium.

Table IV, fifth column, shows the area per cubic centimeter of oil calculated from the number distribution of drops measured in a Stanolax emulsion stabilized by 0.00083 M sodium oleate. This emulsion was not very stable and began to break shortly after measuring. The area per cubic centimeter of Stanolax in such an emulsion when fresh amounts to 9.6×10^3 sq. cm. Equal volumes of all and soap solution were used so, since 1 cc. of 0.00083 M soap solution would contain 0.505×10^{18} molecules, the area associated with one molecule of soap (if all of the soap were in the interface) would be 9.6×10^3 divided by 0.505×10^{18} or 190×10^{-16} sq. cm. This would be the minimum area which could be associated with one molecule of soap in the interfacial area of this emulsion. Since all the soap does not go into the interface the actual area is considerably larger. In comparison it may be noted that the area occupied by one molecule of oleic acid in a closely packed monomolecular film is 20.5×10^{-16} sq. cm.

In general only about 2% of paraffin oil is emulsified by pure water, but with soap as an emulsifying agent a highly concentrated emulsion, with about 75% of oil, is easily obtained by the formation of a highly dilute monomolecular film. The film gives such an emulsion even when it contains only one-tenth to one-fifth as many molecules of the soap as there are molecules of oleic or palmitic acid in a tightly packed monomolecular film. Such an emulsion is not stable, and on standing the area of its interface decreases and the area per molecule of soap in the film decreases, until the area becomes about that for a tightly-packed monomolecular film. Whether the film becomes thicker than this on long standing has not been determined but work on this problem is in progress.

Griffin[9] carried out careful analytical work on emulsions of kerosene

---

[9] Griffin, THIS JOURNAL, **45,** 1648 (1923); see also van der Meulen and Rieman, *ibid.*, **46,** 876 (1924).

and found that the soap film exhibited about half as many molecules (sodium oleate and oleic acid) as are present in a condensed film of oleic acid. His determinations would have been decisive if sufficient work had been done on the distribution of sizes of the droplets in the emulsions; but, since only about 200 droplets in each emulsion were measured, and these were observed in a drop of emulsion suspended from a cover glass, it is evident that the error in the interfacial area may have been very large. However, the areas per cubic centimeter of oil found by him are consistently lower than those obtained by us, so, unless the method of emulsification which he used was much less efficient, the areas which he obtained are probably too low. If this is true, the conclusion which he reaches, that the soap film is monomolecular and of a much lower concentration than a condensed film of the acid, would still be valid.

Table VI gives the area per molecule of soap (sodium oleate or oleic acid) for three emulsions, and minimum, not actual, areas for still others. The minimum areas given are those obtained on the basis of the (incorrect) assumption that all of the soap is in the interface.

TABLE VI

MOLECULAR AREAS POR THE SOAP AT THE INTERFACIAL FILM IN OIL-IN-WATER EMULSIONS (ACTUAL AND MINIMUM AREAS X 10^{16})

Emulsion	First day, min.	Third day, min.	Third day actual	Seventh day, min.	Tenth day, min.	15.5 months, min.
0.00083 M NaOl and Stanolax	190	..	..	..	..	..
0.005 M sodium oleate and octane	84	46"	61[a]	35 6	..	..
0.005 M cesium oleate and octane	82	48	64	30	..	..
0.01 M sodium oleate and octane	32.4	24	50	..	18.3	12.7
0.01 M cesium oleate and octane	32.7	..	..	..	..	..

[a] Determined on the second instead of the third day.

The evidence thus far obtained does not indicate that any of the soap films are thicker than monomolecular.

14. Summary

The distribution of sizes for the droplets in emulsions, both of the oil-in-water and the water-in-oil types, has been determined by a statistical method by the use of a projection apparatus used in conjunction with a microscope.

The following conclusions summarize the results of the work.

1. Within the range of microscopic observation there is no progressive shift in the maxima of the curves which show the distribution of diameter for emulsions made with soaps, as the cation is changed from sodium to potassium and to cesium.

2. In general, the greater the viscosity of the oil the greater the diameter of the largest drops in oil-in-water emulsion, but the peak in the diameter-distribution curve is not shifted.

3. A study of the changes in diameter-distribution, area-distribution and volume-distribution of emulsoid particles with aging gives a more exact method for determining stability than the older method of merely observing the gross features of the emulsion such as the separation of oil in bulk.

4. The method used in preparing an emulsion is one of the factors determining the distribution, but the striking feature of the present work is that the shift of the diameter at the maximum is so slight with the different methods of shaking or stirring employed.

5. The distribution of diameters of the particles of emulsions stabilized by soaps is changed only slightly by the addition of moderate concentrations of oleic acid or of the corresponding base (as of sodium hydroxide to sodium oleate). However, 0.1 M base increased considerably the number of small drops. The stability is, however, usually lessened considerably by the addition, for example, of 0.1 *M* oleic acid to the organic phase, or either 0.1 M sodium hydroxide or 0.1 M sodium chloride to the aqueous phase before the emulsion is formed.

It may be noted that the addition of either sodium hydroxide or sodium chloride to an aqueous-sodium oleate solution of low or moderate concentration greatly lowers the interfacial tension against an oil.

6. Such variations in the hydrocarbon chains of the soaps as were tried had little or no effect upon the distribution, except in the case of *potassium chaulmoograte in which the number of the smallest drops was greatly increased* above that for the oleate or stearate.

7. Magnesium and aluminum soaps gave emulsions of water in oil in which the distribution of sizes is the same, in general, as that found for those of the oil in water types.

8. Exceedingly dilute emulsions made *without* stabilizing agents also exhibit the usual type of distribution, but the drops are much smaller.

9. The area per molecule of sodium oleate in the interfacial film was 61×10^{-16} sq. cm. (61 Å.^{2}) for an emulsion made with 0.005 molar soap. At the time this area was determined, two days after the emulsion was made, the concentration of the soap in the aqueous phase was 0.00105 molar. For emulsions produced by 0.0008 sodium oleate and of Stanolax the molecular interfacial area was *greater* than 190 Å.^{2} according to measurements made within four hours of the time of preparation. It is evident that concentrated emulsions may be produced by means of an interfacial soap film in which the number of molecules of soap is *considerably less* than corresponds to a closely packed monomolecular film. However, the total interfacial area decreases with the time in such cases until finally the film becomes more tightly packed, but the evidence obtained thus far does not indicate that the film becomes thicker than monomolecular.

CHICAGO, ILLINOIS

[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

BY WILLIAM R. CROWELL AND H. DARWIN KIRSCHMAN

RECEIVED JANUARY 21, 1929 PUBLISHED JUNE 5, 1929

. Introduction

Among the problems engaging the attention of this Laboratory is that of a study of the rate of reaction between octavalent osmium and hydrobromic acid. Since the products of this reaction are quadrivalent osmium and bromine, it is apparent that its rate might be measured either by a determination at suitable time intervals of the remaining octavalent osmium, or of the bromine or quadrivalent osmium formed. Previous work on ruthenium[1] and octavalent osmium[2] and preliminary experiments on the potentiometric titration of hydrobromic acid solutions of bromine, octavalent and quadrivalent osmium indicated that trivalent titanium would be a satisfactory reducing agent for this purpose. In these last experiments the titration curve obtained by plotting voltage readings against cubic centimeters of reagent added showed three inflections. The first inflection corresponded to the reduction of the bromine to bromide ion, the second to the reduction of the octavalent osmium to the quadrivalent state and the third to the reduction of the quadrivalent osmium to the trivalent form.

The present paper deals with an investigation of the suitability of trivalent titanium as a reagent for determining one or more of these constituents with sufficient accuracy to warrant its use in the rate experiments. It describes the conditions employed and the results obtained in the potentiometric titration of hydrobromic acid solutions of (1) octavalent osmium, (2) bromine, (3) bromine in the presence of octavalent osmium, (4) bromine in the presence of quadrivalent osmium and (5) bromine, octavalent and quadrivalent osmium when present together.

Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of octavalent osmium with hydrazine sulfate[2] except that provision was made for keeping the reducing agent as well as the titration vessel in an atmosphere of nitrogen.

Hydrobromic acid free of bromine was obtained by distilling the 42-48% acid and retaining the middle portion.

---

[1] Crowell and Yost, THIS JOURNAL, 50,374 (1928).

[2] Crowell and Kirschman, *ibid.*, 51,175 (1929).

The bromine solution was prepared by distilling the c. P. reagent from potassium bromide and sulfuric acid into distilled water.

The stock solutions of osmium tetroxide were prepared as described in the above mentioned article,[2] and were about 0.5 N in potassium hydroxide.

The thiosulfate solution was frequently checked against a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

The titanium solutions were prepared from 1 *N* titanous chloride or sulfate. These were made 0.005–0.01 *N* in trivalent titanium and 0.3 *N* in hydrochloric, hydrobromic, or sulfuric acid. In order to remove traces of hydrogen sulfide, the undiluted acid and reagent were boiled together for one minute before making up to volume. The concentration of these solutions was determined by means of a solution of ferric sulfate which had been standardized against the permanganate solution. Standardizations were made before and after each set of three or four potentiometric titrations and the concentration was usually found constant within 0.1–0.2%. If the change was much greater than this the results obtained were rejected.

Titration of Octavalent Osmium with Titanous Chloride

Definite volumes of the standardized osmium tetroxide solution were titrated with a titanous solution in the presence of sulfuric, hydrochloric or hydrobromic acid. The procedure was as follows: the osmium solution was pipetted into the titration beaker containing about 50 cc. of the acid solution at room temperature, the cover of the beaker placed in position, a volume of titanous solution within 1–2 cc. of that required to reduce the osmium to the quadrivalent state added immediately and nitrogen then admitted slowly (one bubble every two seconds). This procedure was found necessary for accurate work on account of the volatility of the tetroxide. After the octavalent osmium had been reduced to quadrivalent, the nitrogen was bubbled through the solution more rapidly (1–2 bubbles per second). An amount of titanous solution was then added whose volume was within about 1 cc. of that necessary to effect reduction to the trivalent form and the titration continued until well past the inflection point.

The effect of different acids and of variations in the concentrations of these acids upon the color of the osmium solutions is an interesting feature of these titrations. The neutral or slightly acid solutions of octavalent osmium are colorless. When the reduction with titanous ion took place in a sulfuric acid solution, an amber color developed which persisted even after sufficient reagent had been added to reduce the osmium to the trivalent state. With this acid it was possible to obtain only one recognizable inflection in the titration curve, *viz.*, that corresponding to the reduction from the octavalent to the quadrivalent state. On addition of titanium reagent in the presence of hydrochloric acid the solution at first became light yellow, but when five equivalents of reducing agent per gram atom of osmium had been added, the solution became practically colorless. However, only one marked inflection in the titration curve was obtained, that corresponding to the octa–quadrivalent change. With hydrobromic acid (Curve B, Fig. 1) the solution became a deep orange-red as soon as reduction to the quadrivalent form was complete. Further addition of titanous solution produced a gradual change in color to a light yellow and when five equivalents of trivalent titanium per gram atom of osmium had been added, the solution became almost colorless. Two easily recognizable inflections were obtained: one when reduction to the quadrivalent state was complete; the other when reduction to the trivalent form had taken place. Since the most satisfactory drops in potential were obtained in solutions containing the hydrobromic acid, a more detailed study of the influence of the temperature and concentration changes was made with solutions containing this acid.

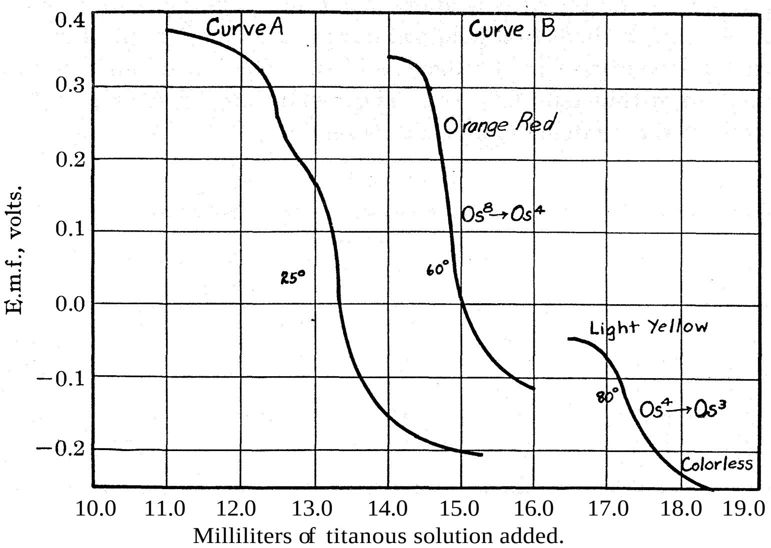


Fig. 1.—Potentiometric titration of hydrobromic acid solutions of octavalent osmium.

The concentration of hydrobromic acid which gave the largest drop in potential at the octa-quadrivalent end-point was found to be about 0.2–0.3 N. At acid concentrations below 0.1 N the solution became amber colored due probably to hydrolysis. At concentrations of acid higher than 0.3 N the drop in potential at this end-point was noticeably smaller and less abrupt. At room temperature a double inflection in the titration curve was obtained (Curve A, Fig. 1), while at 60° a single large drop in potential was obtained (Curve B, Fig. 1). Except in the immediate vicinity of the inflection point the voltage was considered constant when the rate of change was less than 3 millivolts per minute. In the reduction from the quadrivalent to the trivalent state the best inflections were obtained at a temperature of about 80° and at an acid concentration of about

1 *N* (Curve B, Fig. 1). A decided drift upward in the voltage readings was noticed at acidities below 1 *N*. The best results were obtained when the tetroxide solutions were first heated with strong hydrobromic acid in sealed tubes at the temperature of the steam-bath. On diluting these heated solutions to an acidity of about 1 *N* and titrating the quadrivalent osmium at 80°, sharper and greater drops of potential were obtained than when the titrations were carried out at the same temperature and acid concentration but without previous continued heating at 98°. Moreover, there was very little drift in the voltage readings. Results obtained in this manner will be described in more detail in the last section.

Table I contains the results of four typical titrations of a stock solution of octavalent osmium with titanous chloride. The end-points were determined from the inflection points of a curve obtained by plotting voltage against cubic centimeters of reagent added. The inflections could be determined to within 0.02–0.05 cc. The results are compared with those obtained by the modified iodimetric method.[2]

TABLE I

POTENTIOMETRIC TITRATION OF OCTAVALENT OSMIUM SOLUTIONS WITH TITANOUS CHLORIDE

Initial volume = 52–55 cc.

Normality of HBr	OsO_4 soln., cc.	Cc of $TiCl_3$ used		OsO_4 found, millimoles/liter		
		$Os^8 \rightarrow Os^4$ infl.	$Os^4 \rightarrow Os^3$ infl.	$Os^8 \rightarrow Os^4$ infl.	$Os^4 \rightarrow Os^3$ infl.	Iodide method
0.2	4.96	18.30	23.70	6.33	6.56	6.35
.2	4.96	18.28	...	6.30	..	6.35
.3	2.005	9.80	12.25	6.26	6.26	6.35
.4	2.005	10.20	12.90	6.26	6.33	6.35

In the second experiment no satisfactory inflection corresponding to the reduction from quadrivalent to trivalent osmium was obtained. While the third and fourth experiments indicate that the quadri–trivalent break gives as good results as the octa–quadrivalent break, probably the data of the first experiment are more typical, since the general tendency is for the second inflection to give decidedly high results. The results determined from the first inflection point are usually lower than those obtained by the modified iodide method, due probably to loss of the volatile tetroxide during the titration and to the fact that the volatility of tetroxide even from an alkaline solution causes such a rapid decrease in concentration that it is important to make the potentiometric and iodimetric determinations simultaneously. In the later experiments improved technique made this difference much smaller as shown by the results given in Table III.

The Potentiometric Titration of Bromine with Titanous Sulfate

To determine the feasibility of estimating bromine in the presence of hydrobromic acid, octavalent and quadrivalent osmium, four series of experiments were conducted. Since Hendrixson[3] has shown that it is possible to determine bromine potentiometrically in its sulfuric acid solution by means of trivalent titanium, the first series was merely to confirm his results and consisted in the potentiometric titration of sulfuric acid solutions of bromine with the titanous sulfate. The second series was conducted in the presence of hydrobromic acid, the third series in the presence of this acid and 2 cc. of osmium tetroxide solution and the fourth series in the presence of this acid and 2 cc. of quadrivalent osmium solution.

In the first three series the samples of stock bromine solution were pipetted into 50–80 cc. of ice-cold distilled water containing the other constituents. A volume of titanous solution within 1 cc. of that required in a preliminary titration was added immediately and the titration rapidly completed below 5° while nitrogen was bubbled through the solution at the rate of one bubble every two to three seconds. Unless the bromine solution was run into a fairly large volume of cold solution the loss was incredibly high. It was found that if the contents of a 50-cc. pipet was allowed to drain into the empty titration vessel at room temperature and the titration conducted in this solution, the loss was over 10%.

The fourth series of experiments was carried out as follows: a 2-cc. sample of the stock tetroxide solution and 5 cc. of 8 N hydrobromic acid were heated for several hours at 98° in a closed tube. The tube was cooled in an ice-bath, opened under about 40 cc. of ice water, washed into the titration vessel with an additional 40 cc. of ice water and the liberated bromine titrated with the titanous solution. To this quadrivalent osmium solution, which now contained no free bromine, was added a known volume of the stock bromine solution and the titration carried out as before. In these solutions there was always present a small amount of octavalent osmium.[4] During a titration of the bromine the voltage readings became constant to within a millivolt in less than two minutes.

Results of the four series of titrations together with those obtained by the iodide method of bromine determination are recorded in Table II.

The results with sulfuric acid confirm those of Hendrixson. The results also show that bromine can be determined potentiometrically with trivalent titanium in the presence of hydrobromic acid. The average difference between the potentiometric and iodimetric methods in Series 1 and 2 where these acids were present is 0.3–0.4%. In Series 3 where osmium tetroxide was present the percentage difference between the titanous sulfate and iodide–thiosulfate methods varies from about 3% for the highest concentrations of osmium tetroxide and hydrobromic acid to about 0.5%

---

[3] Hendrixson, THIS JOURNAL, 45, 2013 (1923).

[4] This seems to indicate that the osmium is not completely reduced even on protracted heating in concentrated hydrobromic acid but that an equilibrium is reached in which the concentration of octavalent osmium is very small but measurable.

TABLE II

POTENTIOMETRIC TITRATION OF BROMINE SOLUTIONS WITH TITANOUS SULFATE

Volume of bromine solution taken = 25.00 *cc.* Volume of osmium solution taken = 2.005 *cc.* Volume of solution before titration = 87–112 *cc.* Concentration of thiosulfate = 0.03124 N

Series	Acid and concn.	OsO_4 concn. millimoles/liter	Os^4 concn. millimoles/liter	$Ti(SO_4)_3$		Bromine found milliequivalents/liter	
				Normality	Cc. used	Potentiometric	Iodide-thio.
1	1.4 *N* H_2SO_4			0.00845	14.55	4.918	4.910
	1.4 N H_2SO_4			.00845	14.55	4.918	4.910
	0.7 N H_2SO_4			.00845	14.53	4.911	4.910
	Neutral			.00845	15.05	4.935	4.910
2	0.5 *N* HBr			.01053	24.55	10.34	10.40
	0.5 N HBr			.01053	24.60	10.36	10.40
3	0.5 *N* HBr	0.1		.01053	25.20	10.61	10.40
	0.5 *N* HBr	.1		.01053	25.07	10.56	10.40
	0.5 *N* HBr	.5		.01053	25.45	10.72	10.40
	0.2 *N* HBr 1.0 *N* H_2SO_4	.1		.01029	23.54	9.69	9.62
	0.1 *N* HBr	.1		.01053	25.55	10.76	10.71
	0.1 *N* HBr 0.7 *N* H_2SO_4	.1		.01053	25.55	10.76	10.71
	0.1 N HBr	.5		.01048	25.74	10.80	10.71
4	0.27 *N* HBr		0.5	.00896	29.10	10.43	10.42
	0.27 N HBr		.5	,00896	28.95	10.38	10.39

for the lowest concentrations of these substances. In the latter case the concentration of the octavalent osmium is approximately 0.1 millimole per liter, while the concentration of the hydrobromic acid is 0.1 N. The experiments of Series 4 indicate that bromine can be determined without appreciable error in the presence of quadrivalent osmium as high in concentration as 0.5 millimole per liter when the hydrobromic acid is as high in concentration as 0.3 N.

Potentiometric Titration of Bromine, Octavalent and Quadrivalent Osmium in Hydrobromic Acid Solutions Containing All Three Constituents

The next step in the investigation was the determination of bromine, octavalent and quadrivalent osmium in hydrobromic acid solutions containing the three constituents in such proportions as to require on titration suitably large volumes of the reducing agent. These solutions were prepared as follows. Samples of 1.996 cc. of stock tetroxide solution which contained approximately 23 millimoles per liter and 5 cc. of 2.4 N hydrobromic acid were sealed into glass tubes of about 20-cc. capacity and heated at 98° for about three hours. The tubes were then cooled in an ice-bath, broken under about 40 cc. of the ice-cold water, rinsed into the titration vessel with an additional 40 cc. of the cold water and the titrations carried out immediately. As soon as the bromine–bromide ion inflection had been determined, an amount of titanous solution within 1–2 cc. of that necessary to reach the octa–quadrivalent end-point was added immediately. The temperature was then raised to 60° and the titration continued until the $Os^8 \longrightarrow Os^4$ break had been passed. Next, 2.5–8.0 cc. of 8 N hydrobromic acid was added, the temperature was raised to 80° and the quadrivalent–trivalent inflection point was determined. During the titration the nitrogen was bubbled through the solution in the same manner as in the titration of osmium tetroxide. A typical titration curve showing the three inflections is shown in Fig. 2.

The concentration of the stock osmium tetroxide was determined by the modified iodimetric method, care being taken to conduct the potentiometric and iodimetric determinations simultaneously.

The results obtained by the two methods are shown in Table III. For convenience the final results have been expressed in terms of milliequivalents of bromine. On this basis, if amounts of tetroxide are expressed as equivalent bromine, the titration of the 1.996 cc. of tetroxide solution before heating should be equal to the liberated bromine plus the undecomposed tetroxide after heating.

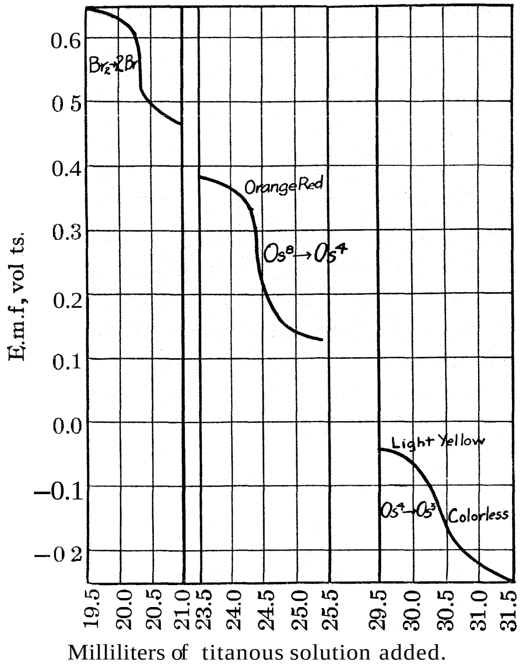


Fig. 2.—Potentiometric titration curve for solution containing bromine, hydrobromic acid, octa- and quadrivalent osmium.

TABLE III

POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTIONS

Volume of OsO_4 solution used = 1.996 cc. Initial volume = 90–100 cc. Initial concentration of HBr in bromine titration = 0.17 *N*. Initial concentration of HBr in OsO_4 titration = 0.15 N. Initial concentration of HBr in Os^4 titration = 0.4–0.8 *N*

Titanous soln., *N*	Titanous solution used $Br_2 \longrightarrow Br^-$, cc.	$Os^8 \longrightarrow Os^4$, cc.	$Os^4 \longrightarrow Os^3$, cc.	Bromine found $Br_2 \longrightarrow Br^-$ Infl., milli-equivalents	Milliequivalents of total bromine calcd. $Os^8 \longrightarrow Os^4$ infl.	$Os^4 \longrightarrow Os^3$ infl.	Iodide method
0.00909	10.00	...	...	0.0909	....	....	0.1837
.00907	9.95	20.24	25.80	0.0903	0.1836	0.1872	.1837
.00906	10.15	20.40	25.95	.0919	.1849	.1882	.1837
.00906	...	20.12	...	....	.1822	....	.1837
.00905	10.20	20.40	...	.0923	.1845	....	.1837

An inspection of Table III shows that for the last four tubes the average deviation of the results of the bromine titrations from the mean is about 0.6%. The general tendency of this bromine value is to increase somewhat. However, the total bromine values (*i. e.*, the free bromine plus the undecomposed tetroxide) are of more significance and are in satisfactory agreement with those obtained by the iodimetric method, the average difference between the latter and the individual potentiometric values being about 0.5%.

It seems evident that it is possible by this method to conduct analyses of solutions in reaction tubes containing the four constituents and obtain results of determinations of bromine and of bromine plus octavalent osmium reliable to within 0.6%. In the rate experiments for which this method is primarily intended, this reliability is quite sufficient. The accuracy can be somewhat increased, if desired, by determining the concentration of the tetroxide solution added to the tubes before heating by potentiometric titration with hydrazine sulfate,[2] titrating only the liberated bromine with the titanous solution, and obtaining the undecomposed tetroxide by difference.

In the experiments where it was possible to obtain fairly good inflections in the curve corresponding to the reduction of the quadrivalent osmium to the trivalent, it will be seen that the values obtained are 2.0–2.5% higher than those obtained by the iodimetric method.

Summary

A method is described for the potentiometric determination of bromine and octavalent osmium in hydrobromic acid solutions containing bromine, octavalent and quadrivalent osmium by titration with solutions of titanous salts. The voltage–cubic centimeter curves obtained show three inflections—the first corresponding to the reduction of the bromine to bromine ion, the second to the reduction of the osmium from octavalent to quadrivalent and the third to the reduction of the quadrivalent osmium to trivalent.

Results reliable to 0.6% were obtained using the first two inflections. The third inflection was not found to be satisfactory for quantitative work.

The potentiometric titration of acid solutions of osmium tetroxide is described and some interesting color changes are noted.

LOS ANGELES, CALIFORNIA

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

THE SOLUBILITY OF GOLD IN MERCURY

BY ARTHUR A. SUNIER AND BRUCE E. GRAMKEE

RECEIVED JANUARY 21, 1929 PUBLISHED JUNE 5, 1929

Although three rather extensive researches on the system gold-mercury have been published[1] within the last ten years, the disagreement in the various results is most remarkable, particularly at lower temperatures. Quite recently rather precise results on the system silver-mercury, using a new type of solubility tube, have been published by Sunier and Hess;[2] it has therefore been thought advisable to redetermine the solubility of gold in mercury using the apparatus just referred to. This paper will present the results obtained on this system between the temperatures 80 and 200".

Materials.—Mercury which had been run through a five foot Meyer column containing mercurous nitrate and distilled in an all-glass apparatus at reduced pressure according to the method of Hulett and Minchin[3] was used in the first three determinations. The mercury collected in the evaporation of amalgams was used for the remaining determinations. Thousand-fine gold foil obtained from the Philadelphia Mint was used in preparing the amalgams of known concentration and in the first few determinations. The gold residues were used to make up the samples for the later determinations.

Apparatus.—The solubility tube, Fig. 1, a modification of the one used by Sunier and Hess, was made of pyrex glass and consisted of the sample tube, A, a capillary filter finely constricted at B, a glass wool filter, C, the upper tube, D, in which the amalgams were prepared and the capillary, E, which is used in the sampling of amalgams. This capillary had a diameter of one-half millimeter.[4]

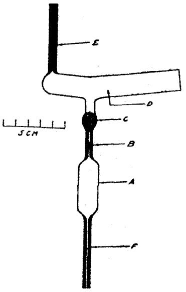


Fig. 1.—Solubility tube.

The solubility tubes were fastened to a rack made of square brass rod and built in a figure H; a side view of the rack is shown in Fig. 2. The tubes in this position are ready for sampling; when turned 180 degrees about the point P the tubes are in the shaking position. The rack (holding four tubes) pivots about the point P and is held in either position by the lock L. The amalgams were shaken by pivoting the vertical rod R in the center and imparting a pendulum-like motion to the tubes on the lower end of the rod of such an amplitude as to completely transfer the amalgams from

---

[1] Parravano, *Gazz. chim. ital.*, (11), *48*, 123 (1918); Braley and Schneider, THIS JOURNAL, **43**, **740** (1921); Britton and McBain, *ibid.*, 48, 593 (1926); Kasanzeff, Ber., 11, 1255 (1878), determined the solubility of gold in mercury at 0, 20 and 100°.

[2] Sunier and Hesq THIS JOURNAL, 50, 662 (1928).

[3] Hulett and Minchin, *Phys. Rev.*, 21, 388 (1905).

[4] There was, of course, the *possibility* that the mercury in the capillary did not become saturated with gold (since diffusion processes alone must be relied upon to accomplish this); then, on breaking the capillary for sampling, this mercury would drop into the main body of the amalgam, causing a dilution effect. Because of this possibility the bore of the capillary was made so small that no appreciable error would be caused if no gold at all was to be found in the small portion of mercury. The excellent agreement of the determinations from both the low and high sides gave added proof that no error arose from this cause.

one end of the tubes to the other. The motion imparted to the rod was obtained by a motor-driven eccentric.

The thermostat, a ten-gallon copper tank heavily lagged, containing heavy cylinder oil, was heated by four 500-watt immersion heaters and agitated by four double paddle stirrers (1000 r.p.m.). Thermal balance was obtained at each temperature by two grid heaters of variable resistance placed on opposite sides of the bath. The mercury thermoregulator operating a 40-watt elongated bulb kept the temperature constant to less than 0.05" over a three-hour period.

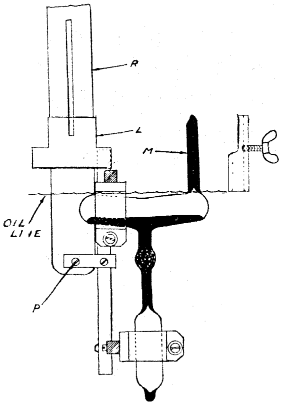


Fig. 2.—Sampling devices.

All temperatures were read from two mercury thermometers graduated in degrees, one standardized by the Physical Laboratory of Taylor Instrument Companies and the other recently standardized by the Bureau of Standards.

Experimental Procedure

The fine capillary, E (Fig. 1), was sealed off and file marked. About 4 cc. of mercury and a 300% excess of gold (using Britton and McBain's data as a guide) were put into the tube, D, which was then sealed off. Capillary F was attached to a Cenco pump, the air evacuated to about 5 mm. and sealed off near the lower end of Tube A.

For a determination of the solubility at a certain temperature, eight tubes were made up and saturation was attained from the low and then from the high temperature side, four tubes being used in each. In the first case the bath was raised to the desired temperature as quickly as possible (requiring at least an hour), the materials were shaken for three hours after thermal balance was obtained and then sampled.

For the corresponding high-side determination the bath was held for three hours at least 5° (sometimes 10 to 15°) above the desired temperature and then allowed to drop back to the determination temperature. This was succeeded by the usual three-hour shaking at constant temperature and sampling. The good agreement is sufficient evidence that equilibrium was attained.

When the tubes were ready to be sampled, the shaker was stopped, the lock L raised and the tubes inverted (with the aid of a brass rod not shown) to the position shown in Fig. 2. The fine capillary was broken at the file mark, M, by means of the apparatus, shown separately in Fig. 2, which is a square brass rod drilled to fit the capillary and fitted with a thumb screw. The capillary is broken by tightening the thumb screw. Both the tipping and breaking devices have greatly facilitated the sampling procedure and have been proved to be very reliable. After filtration the tubes were removed from the bath, wiped clean and cooled. The sample tubes were cut off and the amalgam samples transferred to weighed crucibles.

The evaporation method of analysis for gold was employed, the amalgams being heated in porcelain crucibles placed on iron supports in a large pyrex tube heated by gas. A stream of dry hydrogen was passed through the tube, which was held at about 200" (higher temperatures increase the danger of loss of samples through bumping) until no mercury could be detected with the eye; then the temperature was raised to 500–550° and held there for twelve to sixteen hours in the final runs. The apparatus used is apparently similar to that of Britton and McBain in their Series

III, the percentage of gold running from about 7 to 55% in this series; at lower temperatures and percentages of gold, they used the ferrous ammonium sulfate method of analysis; in neither case is any mention made of the precision of analysis, no blank determinations being recorded. This being the case, considerable preliminary work was done before adopting the evaporation method of analysis; a few of the results obtained will now be presented.

This method of analysis was checked as follows: weighed samples of gold foil heated at 500° for four hours in the stream of hydrogen showed no change in weight; samples of mercury slowly evaporated at 200° and then heated to 500° yielded no weighable residue; lastly, four mixtures of gold and mercury were prepared and the mercury was slowly evaporated at 200°; then the samples were heated to 300° for four hours. Additional heating periods are indicated in Table I. The pieces of gold foil weighed 0.4082, 0.3673, 0.4199, 0.3517 g., respectively; the mercury weighed about 50 g. in each case. The results of this experiment are given in Table I.

TABLE I

EVAPORATION OF MERCURY FROM GOLD–MERCURY MIXTURES

Temp., °C.	Heating period, hours	Percentage of mercury still present in gold			
300	4	6.77	7.14	14.5	6.74
300	4	3.27	3.48	8 38	2 84
400	4	0.76	0.70	2.26	0.43
450	4	0.17	0.23	1.14	0.17

This procedure yielded results 0.2% high, hence in later work (Table II and following) higher temperatures were used with much better results. Merz and Weith[5] found that gold retained about 0.33% of mercury after heating gold amalgams at the temperature of sulfur vapor (445°) for sixty hours.

To test the whole experimental arrangement, four tubes were made up containing weighed amounts of gold and mercury and carried through the entire procedure. Table II shows the excellent results obtained, especially for such a low percentage of gold.

TABLE II

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATIONS

Residues heated for twelve hours at 480°

	I	II	III	IV
Gold foil, g.	0.1221	0.1371	0.1344	0.1219
Atomic % of gold taken	.1821	.2089	.2018	.1830
Atomic % of gold found	.1824	.2099	.2026	.1829

Experimental Results

In Table III will be found complete data for two temperatures, while Table IV summarizes all of the data obtained thus far. Table V gives the

---

[5] Merz and Weith, *Ber.*, 14, 1438 (1881).

solubility of gold in mercury at rounded temperatures and compares these values with those obtained from an empirical equation presented later.

TABLE III

SOLUBILITY OF GOLD IN MERCURY

Complete data for two temperatures

No.	Temp., °C.	Gold at start, g.	Amalgam, g.	Gold, g.	Mercury, g.	Atomic % sol.
1	Low side 101.2	1.2	53.682	0.3660	53.316	0.694
2		1.2	55.241	.3726	54.868	.686
3		1.2	50.465	.3445	50.120	.694
4		1.2	48.152	.3313	47.821	.700
1	High side 101.2	1.2	55.406	.3834	55.022	.704
2		1.2	55.141	.3775	54.763	.696
3		1.2	55.258	.3808	54.877	.701
4		1.2	57.369	.3956	56.974	.701
					Av.	.697
1	Low side 182.3	2.4	29.944	.6951	28.248	2.442
2		2.4	30.355	.7289	29.626	2.442
3		2.4	33.271	.7942	32.477	2.427
1	High side 182.3	2.4	35.230	.8404	34.389	2.426
2		2.4	33.840	.8080	33.032	2.428
3		2.4	30.904	.7400	30.164	2.435
4		2.4	34.347	.8241	33.523	2.440
					Av.	2.434

TABLE IV

SOLUBILITY OF GOLD IN MERCURY (SUMMARY OF EXPERIMENTAL DATA)

No. of detns.	8	8	8	4	8	7	7
Temp., °C.	80.8	101.2	121.7	142.1	159.2	182.3	201.1
At. % sol.	0.467	0.697	1.021	1.482	1.847	2.434	2.875[a]
Av. dev., p.p.t.	12.8	6.4	12.1	1.3	3.4	2.5	24.7

[a] This value is a result of seven determinations made by Mr. O. Fitzsimmons, working in this Laboratory, using the tube developed by Sunier and Hess and evaporating amalgams in a vacuum of 0.003 mm. and flaming the residues. A run at 100.1° using this method of analysis gave results in substantial agreement with those presented here. Both methods of analysis are thus quite satisfactory.

TABLE V

SOLUBILITY OF GOLD IN MERCURY AT ROUNDED TEMPERATURES (FROM LOG N vs. $1/T$ PLOT)

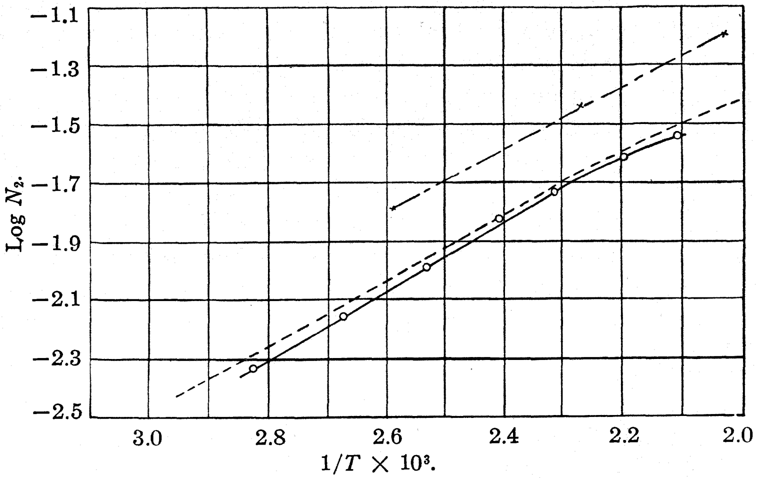
Temp., °C.	80.0	100.0	120.0	140.0	160.0	180.0	200.0
100 N (from curve)	0.459	0.684	0.996	1.385	1.871	2.380	2.849
100 N (calcd.)	0.457	0.688	0.994	1.380	1.864	[a]	[a]
Error, p.p.t.	4	6	2	4	4	[a]	[a]

[a] Equation not valid above 160°.

Of the 48 final determinations only five have been omitted. Of these one was rejected because the deviation was greater than four times the average deviation from the mean for that temperature; the other four constituted the high side at 140° and were rejected because the gold spattered during evaporation; considering the remarkable agreement of the determination from the low side (1.3 p.p.t.) the high-side determination was not repeated. All solubilities are given in atomic per cent. (atoms of gold per 100 total atoms).

Discussion of Results

In Fig. **3** the results are plotted as log N *vs.* $1/T$. It is seen that the values obtained by Parravano and Britton and McBain are greater than those obtained by the authors. The dashed line represents the best line obtained from a plot of Britton and McBain's data, which are on the average 5–10% higher than those presented here. Their analytical procedure, discussed earlier, may account for the high results. The data of Parravano are on the average about 75% high, as compared with those presented here. A fusion method was used by Parravano, so it is difficult to judge where error may have crept in, unless it be due to supercooling which is so likely to give trouble in such cases. Braley and Schneider's results are so very different (and are not plotted in Fig. 3) from the others just mentioned and those presented here, that it seems probable that some serious error was made during the conduct of the research. Kasanzeff's results, obtained so long ago, are indeed remarkable for their probable accuracy; his results are in substantial agreement with those presented in this paper. Kasanzeff pressed his amalgams through chamois skin and also filtered them through a fine capillary; analytical details are rather scanty—indeed the whole article is really an abstract only three paragraphs long.



×——–, Parravano; - - - -, Britton and McBain; —○—, Authors.

Fig. 3.—Solubility of gold in mercury.

A large plot was carefully constructed and used in determining the equation of the straight line, which can be used for temperatures up to 160° only. The equation found is $\log_{10} N = -1167.4(1/T) + 0.966$. The solubility values in Table V were obtained from the large plot and by means of this equation.

It will be noted that when $\log N$ is plotted against $1/T$, the resulting line is not straight at higher temperature. This, it appears, may be true for one or more of three reasons (even though ideal solutions may be in question): (1) the latent heat of fusion of the solid phase is a function of the temperature; (2) the solid phase may not be the one indicated; (3) an actual transition in the solid phase may take place at the temperature where the break occurs. These possibilities will not be discussed at present. If gold amalgams are not ideal solutions the significance of the slope of the $\log N$ vs. $1/T$ curve is rather complicated. Studies along these lines are also under way, not only for amalgams, but other systems. It may be mentioned that some years ago Hildebrand,[6] after a rather thorough research on the vapor pressures of gold and some other amalgams, concluded that the rather large positive deviations from Raoult's law which were encountered might be explained on the assumption of compound formation; more recently,[7] however, the same investigator has said that the gradual accumulation of evidence tends to cast doubt upon this explanation and confirm the theory that internal pressure differences may be largely responsible for such deviations.

Summary

1. A method of preparing and analyzing gold amalgams has been described which yields results 2 parts per thousand high.

2. The solubility tube described earlier has been found suitable (with only slight modification) for the investigation of the system gold-mercury. Fifty-six determinations have been made in the range of temperature 80 to 200°; the present results are considerably lower and the precision of measurement is considerably higher than those previously reported by most other workers.

3. The empirical equation $\log_{10} N = -1167.4(1/T) + 0.966$ expresses the experimental results to 160°, but not above this temperature.

ROCHESTER, NEW YORK

---

[6] Hildebrand, THIS JOURNAL, 35, 501 (1913).

[7] Hildebrand, "Solubility," Chemical Catalog Company, New York, 1924, p. 84 and Chap. XVI.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE CRYSTAL STRUCTURE OF BARIUM

BY A. J. KING[1] AND G. L. CLARK

RECEIVED JANUARY 26, 1929 PUBLISHED JUNE 5, 1929

In 1921 Hull[2] determined the crystal structure of calcium, for which he reported a face-centered cubic lattice with a parameter of 5.56 Å. at room temperature. Prior to the beginning of the investigation here reported the structure of barium and strontium had not been determined, but recently a paper has appeared by Simon and Vohsen[3] presenting the results of their measurement of the lattice structure of strontium, to which they assign a farce-centered cubic structure having a unit edge of 6.03 Å.

Optical measurements of calcium and strontium at room temperature indicate that these metals do not crystallize with cubic symmetry, but with hexagonal symmetry. Since x-ray data do not confirm this, it is possible that a polymorphic transformation occurs above room temperature, leaving the external appearance of the crystals unchanged.

Barium with a purity of 99.9% was used for the x-ray study of this metal. This was prepared by a method described elsewhere.* The samples for x-ray analysis were prepared by pressing the metal into a cylindrical bar in a steel die, then rolling this into a thin foil under dry oil in order to protect the foil from oxidation as far as possible. The foil was cut into narrow ribbons and carefully sealed in pyrex tubes with pure sodium chloride, which served as a standard for the measurement of the diffraction pattern. The sodium chloride and the metal were separated so that their spectrograms were adjacent along the center of the film. Although soft metals are known to recrystallize at room temperature, random orientation of the crystallites was assured by annealing the sample at 120°. Since the spectrograms show no lines which could be ascribed to barium oxide, it is evident that this method of procedure is satisfactory and that oxidation is at most but superficial.

The powder spectrograms were taken with the General Electric x-ray diffraction apparatus. This is provided with a Coolidge x-ray tube containing a molybdenum target and with quadrant cassettes which contain zirconium dioxide filters, so that only the Mo-K, radiation is effective.

The x-ray data agree very well with those for a body-centered lattice with two atoms in the unit cell, the unit edge of which is 5.015 ± 0.003 Å. The relative intensities of the lines compare favorably with those calcu-

---

[1] National Research Fellow.

[2] Hull, *Phys. Rev.*, 17,442 (1921).

[3] Simon and Vohsen, *Z. physik. Chem.*, 133,165 (1928).

[4] A. J. King, "Doctorate Thesis," Syracuse University, 1927; Danner, THIS JOURNAL, 46,2382 (1924); Biltz and Hüttig, *Z. anorg. Chem.*, 114,241 (1920); Dafert and Miklanz, *Monatsh.*, 34,1685 (1913); Guntz and co-workers, *Bull. soc. chim.*, 35,709 (1924).

TABLE I

POWDER PHOTOGRAM OF BARIUM FOIL

Line	Rel. intens.	Calcd. intens., rel.	Plane, *hkl* (*n*)	d_{hkl}, calcd., Å.	d_{hkl}, meas., Å.	a_0, Å.
1	10	10	110(1)	3.5467	3.556	5.028
2	2	2.25	100(2)	2.5085	2.510	5.020
3	7	5.5	112(1)	2.0478	2.050	5.020
4	3	2	110(2)	1.7733	1.773	5.014
5	2	3	130(1)	1.5860	1.584	5.012
6	1	0.75	111(2)	1.4477	1.447	5.013
7	4	4	132(1)	1.3402	1.339	5.014
8	1	2.3	114(1) 110(3)	1.1819	1.181	5.011
9	0.75	2.3	120(2)	1.1214	1.121	5.013
10	1	Weak	233(1)	1.0693	1.069	5.015
11	1	Weak	112(2)	1.0236	1.023	5.012
12	1	Weak	105(1) 134(1)	0.9835	0.983	5.015
13	0.75	V. weak	125(1)	.9157	.915	5.012
14	0.5	V. weak	305(1)	.8600	.860	5.015

$a_0 = 5.015 \pm 0.003$ Å.

lated for this type of lattice. The density, 3.58, calculated from x-ray data further corroborates this assumption and is in harmony with the values 3.66 and 3.64 obtained by actual measurement.[5] The atomic radius of barium is found to be 2.171 Å., whereas the closest approach of the ions of barium in barium fluoride is only 2.684 Å. This is not in conformity with the hypothesis of constant atomic radii, but is of the same magnitude as that of calcium, 1.963 Å., as determined by Hull, and of strontium, 2.131 Å., calculated from the data of Simon and Vohsen.

In view of the disagreement between optical data and x-ray measurements, further studies are being undertaken to ascertain the possible existence of other modifications of the alkaline earth metals at higher temperatures. The work of Simon and Vohsen shows that but one form of strontium exists between room temperature and 100° absolute.

Ebert and Hartmann[6] have recently published the results of their study of the crystal structure of barium. Their results verify those of the authors. A preliminary paper on this subject[7] has apparently escaped their attention.

An investigation of the binary systems calcium–barium, calcium–strontium and barium–strontium is at present under way and will be published in a subsequent paper.

Summary

1. The crystal structure of very pure barium has been found to be body-centered cubic with a parameter of 5.015 ± 0.003 Å.

[5] King, ref. 4; Richards, Hall and Mair, THIS JOURNAL, 50, 3304 (1928).

[6] Ebert and Hartmann, Z. *anorg. Chem.*, 179, 418–420 (1029).

[7] Clark, King and Hyde, *Proc. Nat. Acad. Sci.*, 14, 617–618 (1928).

2. The atomic radius calculated from these data is 2.171 Å. at room temperature.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICS, UNIVERSITY OF ILLINOIS]

PARTIAL MOLAL HEAT CAPACITIES AND RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN SOLUTIONS OF MOLTEN METALS

BY ALBERT N. GUTHRIE AND EARL E. LIBMAN

RECEIVED FEBRUARY 8, 1929 PUBLISHED JUNE 5, 1929

There exist in the literature no data on the partial molal properties of solutions of molten metals. There is likewise a great dearth of experimental work from which such data may be calculated. It seems worth while, therefore, to put on record the following results for the partial molal heat capacities and relative partial molal heat functions of Pb–Sb and Bi–Cd solutions calculated from the work of Wüst and Durrer.[1] By direct calorimetric measurements these investigators have determined the values of the specific heats of the above solutions at different concentrations from which the partial molal heat capacities may be determined. They have also obtained the heats absorbed per gram in going from the pure solid components to the liquid solution at the eutectic temperature, for different concentrations. From these data the relative partial molal heat functions may be calculated.

Relative Partial Molal Heat Functions

Consider a solution made up of components a and b. Let $H = E + PV$ be the total heat function of the solution. Then the partial molal heat function h_a of component a in the solution is defined as $(\mathrm{d}H/\mathrm{d}n_a)_{PTn_b}$ where the n's are the number of moles of the respective components in the solution. If h_a^0 is the value of h_a in some arbitrarily chosen reference state, $\bar{h}_a = h_a - h_a^0$ is called the relative partial molal heat function. It is convenient to choose for the reference state the infinitely dilute solution of a in b.[2]

Consider a system composed of some pure a and some solution. Let some of the a go from the pure phase into the solution. If Q is the heat absorbed by the system, then the molal heat of solution of a is defined as $l_a = (\mathrm{d}Q/\mathrm{d}n_a)_{PTn_b}$. Knowing l_a we may calculate $\bar{h}_a$ from the relation

$$\bar{h}_a = l_a - [l_a]_{n_a = 0} \tag{1}$$

Finally, when $\bar{h}_a$ is known, $\bar{h}_b$ can be calculated from

$$\int_{n_a = 0}^{n_a} \mathrm{d}\bar{h}_b = - \int_{n_a = 0}^{n_a} \frac{n_a}{n_b}\, \mathrm{d}\bar{h}_a \tag{2}$$

---

[1] "Forschungsarbeiten auf dem Gebiete des Ingenieurwesens," Heft 241 (1922).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 87–95.

Let us now fix ow attention upon a system of two components completely miscible in the liquid state, completely immiscible in the solid state. Such a system has a definite eutectic temperature. Let L be the heat absorbed when one mole of b and n, moles of a go from the pure solid state at atmospheric pressure and eutectic temperature into the liquid state to form a solution. Then if λ_a and λ_b are the molal heats of fusion, at the eutectic temperature, of *a* and b

$$L = \lambda_b + \lambda_a n_a + \int_{n_a = 0}^{n_a} l_a \mathrm{d}n_a \qquad (3)$$

and

$$\left(\frac{\mathrm{d}L}{\mathrm{d}n_a}\right)_{PTn_b} = \lambda_a + l_a \qquad (4)$$

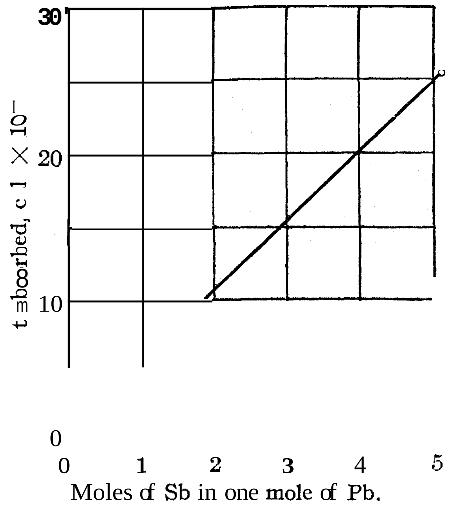


Fig. 1.—Relative partial molal heat functions in Pb–Sb solutions at eutectic temperature.

Values of L are given by Wiist and Durrer in the article mentioned, for different concentrations. Plotting L against n_a and drawing tangents, values of l_a may be determined by (4). As shown in Figs. 1 and 2, the L-n, curves for the systems Pb-Sb and Bi-Cd are straight lines. Thus $(\mathrm{d}L/\mathrm{d}n_a)_{PTn_b}$ is, in each case, a constant, independent of the concentration, and by (4) the heats of solution for these systems are likewise constant, independent of the concentration. Then by (1) and (2) the relative partial molal heat functions at the eutectic temperature are strangely enough zero for these solutions at all concentrations (Tables I and 11).

Partial Molal Heat Capacities

Let C_p he the total heat capacity of a solution of components a and *b*. Then the partial molal heat capacity of *a* is defined as $c_{pa} = (\mathrm{d}c_p/\mathrm{d}n_a)_{PTn_b}$. The data of Wüst and Durrer give the specific heats for the solutions Pb–Sb and Bi–Cd

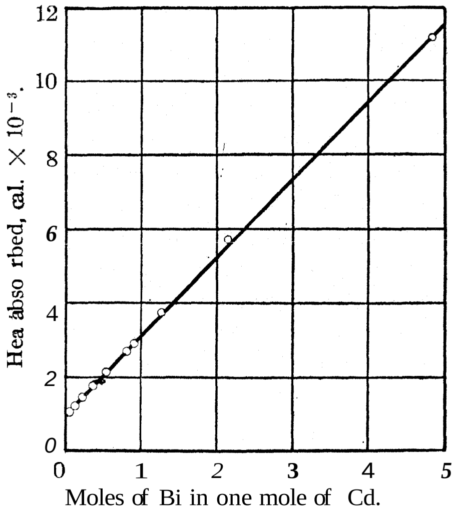


Fig. 2.—Relative partial molal heat functions in Bi–Cd solutions at eutectic temperature.

TABLE I

RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN PB–SB SOLUTIONS AT EUTECTIC TEMPERATURE

Sb, %	Mole frac. of Sb	G = gesamte Warmeeffekte"	n_{Sb} = moles of Sb	Wt. of soln.	L = heat absorbed	$(dL/dn_{Sb})_{PTn_{Pb}}$	$\bar{h}_{Sb}$	$\bar{h}_{Pb}$
7	0.114	8.05	0.128	222.8	1794	4760	0	0
13	.203	9.08	.254	238.2	2165	4760	0	0
25	.362	13.40	.567	276.3	3705	4760	0	0
50	.630	22.76	1.70	414.4	9430	4760	0	0
75	.836	30.55	5 10	828.8	25300	4760	0	0

[a] Wust and Durrer.

L = G X wt. of solution

TABLE II

RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN BI–CD SOLUTIONS AT EUTECTIC TEMPERATURE

Ri, %	Mole frac. of Bi	G = gesamte Warmeeffekte[a]	n_{Bi} = moles of Bi	Wt. of soln	L = heat absorbed	$(dL/dn_{Bi})_{PTn_{Cd}}$	$\bar{h}_{Bi}$	$\bar{h}_{Cd}$
10	0.056	8.44	0.054	123.8	1045	2160	0	0
20	.118	8.61	.134	140.5	1210	2160	0	0
30	.187	8.98	.230	160.6	1443	2160	0	0
40	.263	9.47	.358	187.3	1775	2160	0	0
50	.350	9.47	.538	224.8	2130	2160	0	0
60	.446	9.69	.807	281.0	2695	2160	0	0
63	.477	9.55	.916	304.0	2900	2160	0	0
70	.556	10.02	1.257	374.7	3755	2160	0	0
80	.682	10.16	2.145	562.0	5705	2160	0	0
90	.828	9.92	4850	1124.1	11150	2160	0	0

[a] Wiist and Durrer.

L = G X wt. of solution.

TABLE III

COMPARISONS OF DATA

Component		Bi		Cd		Pb	Sb
Temperature, °C.		300	1000	300	1000	700	700
Specific heat	Calcd.	0.0344	0.0416	0.0733	0.0823	0.0337	0.0547
	Obs. (ref. 4)	.0345	.0419	.0733	.0823	.0338	.0550

TABLE IV

PARTIAL MOLAL HEAT CAPACITIES IN PB–SB SOLUTIONS

Pb, %	25	50	75	87	93
Mole fraction of Pb	0.164	0.370	0.638	0.797	0.886
Sp. heat of the soln.. 700°C."	.0491	.0443[b]	.0387	.0367	.0351
Partial specific heat, 700°, all concns.		Pb,	.0337	Sb,	.0547
Partial molal heat capacity, 700°, all concns.		Pb,	6.98	Sb,	6.66

[a] Wiist and **Durrer.**

[b] In the original article some error was made in the calculation of this value and it has been recalculated from the experimental data.

for different weight per cents. These are plotted in Figs. 3 and 4. The tangents to these curves at any concentration intersect the axes at points representing the partial specific heats of the components.[3] For the systems considered the curves are straight lines and so the partial specific heats, and also the partial molal heat capacities, are constant, independent of the concentration and equal to the molal heat capacities of the pure components in the liquid state. This circumstance affords a means of checking the results by comparison with data obtained by Wüst, Meuthen and Durrer[4] from the pure components (Table III).

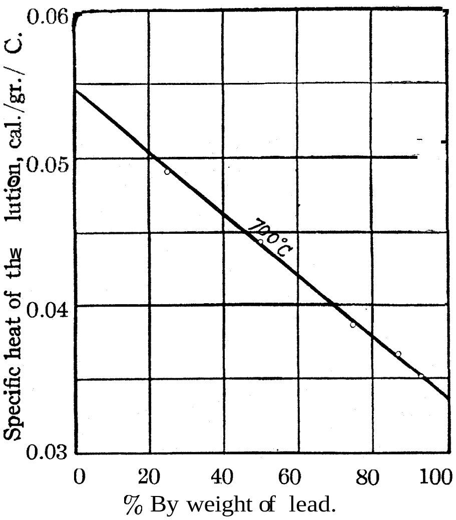


Fig. 3.—Partial molal heat capacities in Pb–Sb solutions.

In making use of the valuable data obtained by these investigators, it is to be noted that some errors have been made in the calculations. Thus Table 29 on the true specific heats of lead, above the melting point, is in error and should be recalculated directly from the experimental data given in the article. Unfortunately the errors noted have been reproduced in the "Handbook of Chemistry and Physics"[7] published by the Chemical Rubber Publishing Co., the Smithsonian Physical Tables (7th edition), and perhaps elsewhere.

We have seen that the partial molal heat capacities of Bi–Cd are constant and equal to the molal heat capacities of the pure liquid components both at 300 and 1000°. It is reasonable to assume that this is true for all temperatures. If we do so we may readily calculate the relative partial molal heat functions at temperatures other than that of the eutectic.

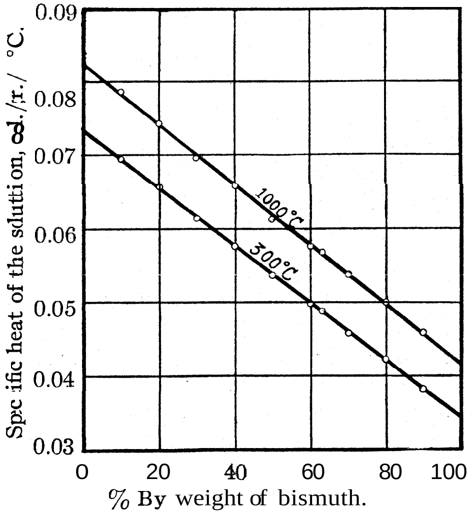


Fig. 4.—Partial molal heat capacities in Bi–Cd solutions.

We have $(\mathrm{d}h_a/\mathrm{d}T)_p = c_{pa}$ and $(\mathrm{d}h^0_a/\mathrm{d}T)_p = c^0_{pa}$, so that $(\mathrm{d}h_a/\mathrm{d}T)_p = [\mathrm{d}(h_a - h^0_a)/\mathrm{d}T]_p =$

---

[3] Lewis and Randall, ref. 2, p. 38.

[4] Ref. 1, Heft 204 (1918).

TABLE V

PARTIAL MOLAL HEAT CAPACITIES IN BISMUTH-CADMIUM SOLUTIONS

Bi, %	Bi, mole fraction	Sp. ht. of soln.[a] 300 °C.	Sp. ht. of soln.[a] 1000 °C.
10	0.056	0.0695	0.0785
20	.118	.0656	.0743
30	.187	.0614	.0695
40	.263	.0576	.0659
50	.350	.0536	.0614
60	.446	.0499	.0576
63	,477	.0489	.0569
70	.556	.0459	.0537
80	.682	.0422	.0500
90	.828	.0382	.0459

		Partial specific heat, all concentrations
Bi	300 °C.	0.0344
	1000 °C.	0 0416
Cd	300 °C.	.0733
	1000 °C.	.0823

		Partial molal heat capacity, all concentrations
Bi	300 °C.	7.20
	1000 °C.	8.69
Cd	300 °C.	8.24
	1000 °C.	9.25

[a] Wüst and Durrer.

$c_{pa} - c^0_{pa}$. But on the assumption just made $c_{pa} - c^0_{ap} = 0$, and we have $(d\bar{h}_a/dT) = 0$. From this we see that $\bar{h}_a$ is independent of the temperature. Thus not only at the eutectic temperature but at all temperatures the relative partial molal heat functions of the components are zero at all concentrations.

Conclusions

1. The relative partial molal heat functions of the components of the systems Pb–Sb and Bi–Cd have been calculated for the eutectic temperatures. They are found to be equal to zero independent of the concentrations.

2. The partial molal heat capacities of the components of the system Pb–Sb have been calculated at 700° and have been found to be constant and equal to the molal heat capacities of the pure liquid components. The same calculation has been performed for the system Bi–Cd at the temperatures 300 and 1000° and in each case the partial molal heat capacities have been found to be constant, independent of concentration and equal to the molal heat capacities of the pure components.

3. Assuming that the partial molal heat capacities are the same as the molal heat capacities of the pure liquid components, not only at the temperatures for which this has been verified but at all others, it is shown that the relative partial molal heat functions are zero not only at the eutectic temperature but at all others.

URBANA, ILLINOIS

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

THE THERMAL REACTION BETWEEN POTASSIUM OXALATE AND MERCURIC CHLORIDE

BY W. E. ROSEVEARE AND A. R. OLSON

RECEIVED FEBRUARY 11, 1929 PUBLISHED JUNE 5, 1929

The oxidation of oxalates by mercuric chloride as expressed by the following equation

$$2HgCl_2 + C_2O_4^{--} = Hg_2Cl_2 + 2Cl^- + 2CO_2$$

has been studied by a large number of investigators during the past seventy-five years. It is not surprising that the conclusions drawn by the various investigators should be lacking in agreement, since the reaction is influenced by both positive and negative catalysts. The reaction is sensitive not only to heat, but also to light of a frequency range extending all the way from the visible to the very hard x-rays. The present investigation, which deals with the thermal reaction in neutral aqueous solutions, is the first section of a more general investigation of this reaction.

Methods **of** Measuring the Rates of Reaction.—Two methods were used for making the kinetic measurements. The first consisted in sealing the reacting solutions in pyrex flasks, which were kept in a thermostat at the desired temperature for definite lengths of time, after which they were removed from the thermostat and quickly plunged into cold water. The bulbs were broken open and the amount of mercurous chloride formed was determined gravimetrically. In some cases, however, the amount of mercury remaining in solution was determined by precipitating as sulfide.

A second method was used where samples for analysis were drawn at different times from the same solution. This method involved the use of the apparatus shown in Fig. 1, which consists of a one and one-half liter pyrex bulb with a 1-mm. capillary sealed in through the top and extending to 0.5 cm. from the bottom. A is an all-glass condenser about 12 cm. long, through which the capillary passes to the capillary stopcock. Inside the condenser the capillary is thin walled to facilitate the rapid cooling of the contents while a sample is being taken. The tube B was used to introduce the reaction mixture, after which it was sealed off at the constriction. The bulb was immersed in a thermostat up to the point C. Water was passed through the condenser jacket and through a coil of copper tubing which was placed around the stopcock to keep the stopcock grease from melting and blowing out, but which could be removed when a sample was to be withdrawn. The vapor pressure of the water and carbon dioxide in the bulb gave a total pressure of about two atmospheres, which forced the solution out through the capillary when the stopcock was opened.

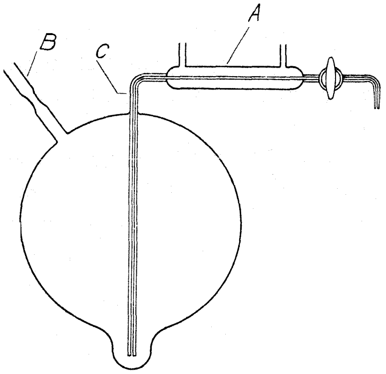


Fig. 1.

Before taking a sample, sufficient solution was run out to wash out the capillary and then the sample was taken in a test-tube, which was cooled to room temperature in a water-bath A five or ten-cc. portion was measured out with a pipet, filtered free of mercurous chloride and acidified with hydrochloric acid to prevent any further reaction. The solutions were analyzed for mercury by precipitating with hydrogen sulfide and weighing as sulfide. The reaction vessels were always cleaned with hot chromic acid which was followed by hot concentrated hydrochloric acid to insure the removal of traces of iron. It was found that the results were more reproducible when the hydrochloric acid was used. The potassium oxalate, potassium chloride and mercuric chloride used were all twice recrystallized from the C. P. materials, whose analyses were given as containing **0.001%** iron. The solutions were made up with ordinary distilled water.

The "zero" of time, in this method of measuring the rate, was not taken as the time when the apparatus was placed in the thermostat, but was taken as the time when the first sample was withdrawn, which was about half an hour after placing it in the thermostat. In this way the effect of the lag in coming to the temperature of the thermostat was avoided. Measurements by both methods were carried out in a paraffin thermostat regulated to within 0.1° at 100° and **0.15**" at 120°. The solutions were mixed and analyzed in dim artificial light but at other times were kept in the dark.

The Reaction in the Absence of Oxygen.—The reaction is sensitive to very small traces of oxygen and so it was necessary to use great care to insure its removal. The oxygen was removed by saturating the solutions with pure carbon dioxide at atmospheric pressure and then the carbon dioxide was boiled out of the solutions under reduced pressure, carrying the oxygen with it. This process was repeated six times, giving solutions with much less oxygen than could be obtained by passing oxygen-free carbon dioxide through the solutions for six hours. The bulbs were then filled with purified carbon dioxide to atmospheric pressure at *25*° and sealed off. The carbon dioxide was freed from oxygen by passing it through copper turnings heated to 400°. In spite of these precautions, there appeared to be sufficient oxygen left to affect the rate. This was the principal cause of the difficulty in obtaining reproducible results.

The Effect of the Mercuric Chloride.—The order of the reaction with respect to mercuric chloride was determined by using a solution where the amount of potassium oxalate was equivalent to about ten times the quantity of mercuric chloride present. Under these conditions the total observed order of the reaction would be that of the mercuric chloride. Table I shows the results of such an experiment made by the second method where samples were drawn from the same solution.

TABLE I

100°; ATM. **PRESSURE OF** CO_2; KCl, **0.0909** *M;* $K_2C_2O_4$, **0.405** *M;* $HgCl_2$, **0.0836** M

Minutes	0	65	143	262	428	549	
HgS (5 cc.)	0.0819	0.0751	0.0672	0.0567	0.0466	0.0374	
−Log HgS	1.087	1.124	1.173	1.246	1.351	1.427	
K (1st order) × 10^5		57	60.2	60.7	61.7	61.9	Mean, 61

This shows that the velocity of the reaction is very nearly proportional to the first power of the total mercury in solution. No correction was made for the retarding effect of chloride ion formed in the reaction. If such a correction were made it would give an upward trend to the constants, making it appear less than first order. Such a trend may be explained as due to the increased dissociation of Hg_2Cl_4[1] which would occur when the $HgCl_2$ is used up in the reaction.

The Effect of Chloride Ion.—When chloride ion is added to the solution the rate of reaction is decreased. Tables II and III give results when the chloride-ion concentration is large compared to the concentration of the mercuric chloride. The two parts of each table represent duplicate experiments using the large bulb.

TABLE II

100°; ATM. PRESSURE OF CO_2; KCl, 0.3636 *M*; $K_2C_2O_4$, 0.405 *M*; $HgCl_2$, 0.0836 *M*

Minutes	HgS (10 cc.)	−Log HgS	*K* (1st order)
0	0.1863	0.7298	
507	.1399	.8542	24.5 × 10^{-5}
979	.1105	.9566	23.2 × 10^{-5}
2077	.0735	1.1337	19.5 × 10^{-5}
0	.1915	0.7178	
507	.1381	.8598	28.0 × 10^{-5}
979	.1050	.9788	26.7 × 10^{-5}
2077	.0673	1.1720	21.9 × 10^{-5}
		Mean,	24.1 × 10^{-5}

TABLE III

SAME AS TABLE II EXCEPT KCl, 0.7272 *M*

Minutes	0	346	1030	1752	0	1030	2595	
HgS	0.1929	0.1816	0.1662	0.1535	0.1910	0.1659	0.1447	
−Log HgS	0.7147	0.7409	0.7794	0.8139	0.7190	0.7801	0.8395	
K (1st order) × 10^5	....	7.6	6.3	5.7	....	5.9	4.6	Mean, 6

It will be observed that the mean rate in Table II is almost exactly four times that in Table III. Since the chloride ion is in large excess and the concentration is doubled in the latter, it is evident that the rate varies as the inverse second power of the chloride-ion concentration when the latter is large. The mercury, under these conditions, is nearly all present as $HgCl_4^{--}$ as shown by the equilibrium $(HgCl_2) = k(HgCl_4^{--})/(Cl^-)_2$. Therefore, the rate is proportional to the concentration of the $HgCl_2$ molecules under all conditions, the chloride-ion concentration only affecting the concentration of the $HgCl_2$.

There is a marked downward trend in Tables II and III which can be accounted for by the retarding action of the chloride ion formed during the reaction. The retarding effect of the chloride ion formed during the reaction is greater, the larger the initial chloride-ion concentration. This

---

[1] G. A. Linhart, THIS JOURNAL, 37, 271 (1915).

is because there are, for each atom of mercury reduced, three times as many chloride ions formed when the chloride-ion concentration is large as when it is small. The main reaction for very large and very small ion concentrations may be represented as $HgCl_4^{--} + (-) = {}^1/_2Hg_2Cl_2 + 3Cl^-$ and $HgCl_2 + (-) = {}^1/_2Hg_2Cl_2 + Cl^-$. We do not know the dissociation constant of $HgCl_4^{--}$ at 100°; therefore we cannot make an accurate correction for the retarding effect of the chloride ion formed. However, a calculation was made assuming a negligible dissociation and this fully accounted for the trend in Table II and for half the trend in Table III.

The Effect of the Oxalate.—The effect of the oxalate concentration was determined using an excess of oxalate with a solution similar in every respect to the solution in Table I except that the oxalate concentration was made exactly one-half as large. The results for this solution listed in Table IV give a mean of 14×10^{-5}. The mean of Table I is 61×10^{-5}.

TABLE IV

AT 100°; ATM. PRESSURE OF CO_2; KCl, 0.0909 *M;* $K_2C_2O_4$, 0.2025 *M;* $HgCl_2$, 0.0836 M

Minutes	0	118	353	702	1293	
HgS	0.0924	0.0893	0.0831	0.0754	0.0574	
—Log HgS	1.034	1.049	1.080	1.123	1.241	
K (1st order) $\times 10^5$	....	13	13	13	16	Mean, 14

This value is equal to four times the mean value in Table IV. Since the oxalate concentration in Table I is twice that of the oxalate in Table IV, the rate varies as the second power of the oxalate concentration.

The power of the oxalate in the kinetic equation was also determined under conditions where the mercuric chloride was in excess, by the method of sealed bulbs. In this case the total observed order of the reaction will be that of the oxalate since there will be only a negligible change in the mercury concentration.

TABLE V

120"; CO_2 PUMPED OFF BEFORE SEALING; KCl, 0.05 M; $K_2C_2O_4$, 0.0100 *M;* $HgCl_2$, 0.0989 M

Minutes	0	780	1481	3856
Hg_2Cl_2	.....	0.0323	0.0517	0.0773
$(a - x)$	0.00100	0.00726	0.00558	0.00345
$1/(a - x)$	100	138	179	290
K (2d order)	.....	0.049	0.053	0.050

TABLE VI

120°; CO_2 PUMPED OFF BEFORE SEALING; $HgCl_2$, 0.0989 *M;* $K_2C_2O_4$, 0.00997 *M*

Minutes	0	405	606	2140
Hg_2Cl_2	.....	0.0396	0.0493	0.0855
$(a - x)$ mole/liter	0.00997	0.00664	0.00576	0.002758
$1/(a - x)$	100.3	150.6	173.6	363.0
K (2d order)	.....	0.124	0.121	0.123

These results are given in Tables V and VI. Potassium chloride was added to the former but not to the latter. In both cases, however, the rate obeys a second-order law, showing that the rate is proportional to the second power of the oxalate concentration when the mercuric chloride is large as well as when the oxalate is in excess.

The Reaction in the Presence of Oxygen.—Oxygen not only retards the reaction but changes the order of the reaction with respect to the oxalate. This change depends on the pressure of oxygen and upon the concentration of the reactants. It was necessary to measure the rates in short enough time intervals so that we could neglect the change of concentration of the reaction materials. In Table VII the quantity of oxygen is stated in terms of millimoles of oxygen admitted to the flasks.

TABLE VII

100°; $K_2C_2O_4$, 0.200 M; $HgCl_2$, 0.12 M; KCl, 0.100 M

Oxygen	0.223	0.446	0.892	1.784	3.568
Minutes	60	60	255	255	255
Hg_2Cl_2, g.	0.1318	0.0798	0.1516	0.1085	0.0847
Rate, Hg_2Cl_2/min.	0.00220	0.00133	0.00059	0.00043	0.00033
Rate, calcd.	0.00222	0.00120	0.00069	0.00043	0.00031

The concentration of oxygen in solution would be proportional to this quantity, since the volume of each flask was 152 cc. After 50 cc. of the solution was placed in each flask the air was pumped out and the stated amount of oxygen admitted before sealing off. For the lower concentrations of oxygen the rate is nearly inversely proportional to the oxygen concentration, but at higher concentrations of oxygen its effect is much less. Analyses of the gas remaining in the flasks as well as of the resulting solutions showed that the oxygen did not oxidize determinable amounts of the oxalate.

The rate here may be best expressed by the equation

$$\frac{dx}{dt} = \frac{1}{k'(O_2)} + k'' \tag{1}$$

If k' is assumed to be 22×10^2 and k'' to be 18×10^{-5}, one obtains the calculated values of the rate given in the last column of Table VII. In Fig. 2 the experimental rates are given by the circles while the calculated values fall identically on the curve. This shows that the calculated values obtained from the above equation lie on the best smooth curve drawn through the experimental points.

The Effect of the Mercuric Chloride with Oxygen Present.—The order of the reaction was determined using an excess of oxalate so that the total observed order was that of the mercuric chloride.

The results obtained by the method of small flasks are given in Table VIII, which shows that the rate of the reaction is proportional to the first power of the concentration of the mercuric chloride. The retarding effect

Table VIII

100°; Atm. Pressure of O_2 when at 25°; Trace of CO_2; $K_2C_2O_4$, 1.796 *M;* $HgCl_2$ 0.0968 M

Minutes	0	206	450	974	1464	1890
HgS	0.2255	0.1794	0.1414	0 0904	0.0554	0 0394
−Log HgS	0.6468	0.7462	0.8495	1.0438	1 2565	1.4045
K (1st **order**) × 10^5		48	45	41	42	40

of the chloride ion formed in the reaction is sufficient to account for the downward trend in the rate constants. With oxygen present it is impossible to determine the effect of chloride ion when the latter is in excess, since then the rezction is immeasurably slow.

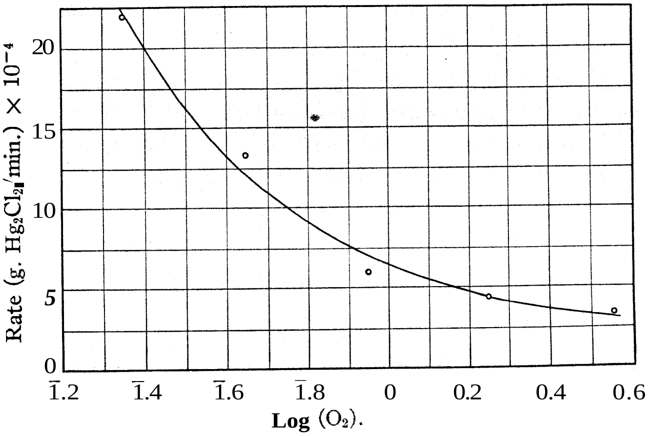


Fig. 2.

The Effect of the **Oxalate with** Oxygen Present.—The order of the reaction with respect to the oxalate was determined by using a solution similar to that in Table VIII in every way except that the concentration of the oxalate was one-half as great.

Table IX

Same as Table VIII except $K_2C_2O_4$, 0.898 *M*

Minutes	0	1149	1460	2997
HgS	0.2255	0.1155	0.0985	0 0533
−Log HgS	0.6468	0.9374	1.0066	1.2733
K (1st **order**) X 10^5	....	25.3	24.6	20.9

The results given in Table IX show a rate that is one-half the rate in Table VIII; therefore the rate is proportional to the first power of the concentration of the oxalate.

The Effect of Iron Salts.—The effect of oxygen depends on the amount of iron salts present in the solution. The addition of one part of ferrous salt to 100,000 parts of mercuric chloride will change the order of the reaction with respect to the oxalate from second to first when an appropriate concentration of oxygen is present. This accounts for the results of Dahr,[2] who found that the rate varied as the first power of the oxalate concentration in solutions made from C. P. materials when saturated with carbon dioxide. Table X shows that the reaction is first order with respect to the oxalate when a small amount of iron salt is added, even when the pressure of the oxygen was too small to measure with an ordinary manometer.

TABLE X

120°; TRACE OF O_2; $HgCl_2$, 0.100 *M*; $K_2C_2O_4$, 0.0100 M; $FeCl_3$, 0.004 M

Minutes	0	360	653	1448
Hg_2Cl_2	....	0.0363	0.0583	0.0900
(a − x), mole/liter	0.0100	0.00693	0.00506	0.00238
−Log (a − x)	2.000	2.159	2.296	2.623
K (1st order) X 10^5	....	44	45	43

Ordinary C. P. mercuric chloride and potassium oxalate, in which the analysis as stated on the container admitted 0.001% iron, also were found to give a rate proportional to the first power of the oxalate concentration. This appears to be due to the iron salts contained in them since the recrystallized chemicals react with a rate proportional to the second power of the oxalate concentration under the same conditions.

Discussion and Summary

The experimental results may be summarized by the equation

$$\frac{dx}{dt} = \frac{k_1(HgCl_2)(C_2O_4^{--})^2}{k_2(O_2) + k_3} + \frac{k_4(HgCl_2)(C_2O_4^{--})(Fe^{++})^x(O_2)^z}{k_5(O_2)^z + k_6}$$

k_3 is necessary in order that the rate does not approach infinity as the concentration of oxygen is continually decreased. It is so small, however, that it could be neglected in all experiments where oxygen was admitted. Under all conditions the rate is proportional to the concentration of the $HgCl_2$ molecules. Chloride ion does not occur in the equation since it changes only the concentration of the $HgCl_2$ by forming $HgCl_4^{--}$. When the concentration either of oxygen or ferrous ion is large the first term can be neglected and the rate will be proportional to the first power of the oxalate concentration. On the other hand, when the concentration of the oxygen is very small, the first term is large and the second term can be neglected, making the rate proportional to the second power of the oxalate concentration. When the concentration of the mercuric chloride, oxalate and ferrous ion is constant the rate will be given by

$$\frac{dx}{dt} = \frac{1}{k_2'(O_2) + k_3'} + \frac{k_4'(O_2)^z}{k_5(O_2)^z + k_6}$$

However, k_3 and k_6 are so small that they may be neglected in all the experiments where oxygen was present. Then the equation reduces to

$$\frac{dx}{dt} = \frac{1}{k_2'(O_2)} + k_4''$$

---

[2] N. R. Dahr, J. *Chem. Soc.*, 111, p. 752 (1917)

which was found to be true experimentally. The presence of two terms in the kinetic equation indicates that there are two reactions proceeding simultaneously, the total rate being the sum of the two separate rates. Winther[3] studied the effect of ferrous salts on the reduction of mercuric chloride by ammonium oxalate in the presence of oxygen at room temperature. He found that the oxidation of ferrous oxalate by oxygen induced the reaction to take place, giving as many as 4000 molecules of mercurous chloride per molecule of ferrous oxalate oxidized by oxygen, but this number decreased with increasing oxygen concentration. However, there was no reaction when oxygen was absent. It is evident that the reaction observed by Winther must take place at 100° when oxygen and iron are present, even though in very small amounts. In the present investigation it was found that ferric oxalate decomposes into ferrous oxalate and carbon dioxide at 100" at a moderate rate, so that there will be repeated oxidation of the ferrous iron by oxygen and reduction of ferric iron by oxalate. The first part of each cycle would cause a chain of some 4000 molecules of mercuric chloride to react with oxalate. The repetition of this cycle would account for the catalytic effect of such small quantities of iron. The quantity of oxygen consumed would be equivalent to less than one-thousandth of the oxalate or mercuric chloride reacting, which agrees with the experimental fact that practically no oxygen was used up in the reaction. The effect of iron is too complex to be expressed analytically at the present time as the fraction of the iron present in the ferrous form depends on the concentrations of oxygen and oxalate in the solution, even when one assumes that the steady state is quickly attained.

In the investigation of the photochemical reaction now in progress, the quantum efficiency has been found to be 3000 molecules reacting per quantum of light absorbed. It also is inhibited by oxygen. Dahr[4] has found that the reaction is induced by many oxidizing agents in the dark, giving as many as several thousand molecules of mercurous chloride per molecule of inductor transformed.

The effect of oxygen, therefore, must be three-fold: (a) the inhibiting effect in the first term as shown by the equation, (b) the oxidation of ferrous oxalate to ferric oxalate, thus increasing the number of chains in the second term, and (c) the shortening of the average length of the chain in the second term corresponding to a similar effect in the first term. From these considerations and the fact that the rate becomes independent of the oxygen concentration as the later is increased (see Equation 1), it seems evident that oxygen must occur in both numerator and denominator of the second term to the same power. At the low concentrations of oxygen which would be necessary to determine k_6, the value of the first term

---

[3] Chr. Winther, *Z. Wiss. Phot.*, 7, 411 (1908).

[4] N. R. Dahr, *Ann. chim.*, 11, 197 (1919).

of the rate equation is so great as to make such a determination impossible. On the other hand, if the concentration of the ferrous salt is made large, the retarding effect of the resulting ferric ion, which was observed by Winther, will be large in comparison to k_6. When the concentration of oxygen is large, k_6 and the first term of the equation may be neglected. Under these conditions the oxygen cancels out of the second term and the rate is independent of the oxygen concentrations.

The discussion of the mechanism of the chains occurring in these reactions will be postponed until more work has been done on the reaction in acid solution and on the photochemical reaction.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE ALFRED LEE LOOMIS LABORATORY OF TUXEDO, NEW YORK, AND THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES
II. A STUDY OF EMULSIFYING ACTION

BY WILLIAM T. RICHARDS

RECEIVED FEBRUARY 16, 1929 PUBLISHED JUNE 5, 1929

One of the most spectacular manifestations of the effects of the high frequency sound waves produced by Wood and Loomis[1] is their emulsifying action on benzene, paraffin and even mercury in contact with water. Since this action promises to be of some practical value and since, moreover, it gives important indications of the nature of sound wave effects, it has been briefly investigated.

1. The Mutual Emulsification of Two **Liquids.**—When benzene and water are placed in a test-tube which has been previously wet with water and the tube is irradiated with intense sound waves of 300 K.C., the benzene layer at once becomes cloudy, the water layer more slowly so and, finally, the boundary between the two disappears. A similar action may be observed between water and any other liquid of similar physical properties; even medicinal paraffin follows the same course. With high intensities of sound the agitation of the interface is, however, so intense that reliable observation of the locality at which emulsification occurs is impossible.

In order to verify the suspicion that emulsifying action occurs primarily at the wall in contact with benzene and not at the liquid–liquid interface, very low intensities of sound (roughly one-tenth of those employed by Wood and Loomis, and the author and Loomis,[2] and designated by the latter 100%) were used, and the following results obtained.

In water-wet tubes containing a benzene–water interface the white

---

[1] R. W. Wood and A. L. Loomis, *Phil.* Mag., [vii] 4, 417 (1927).

[2] W. T. Richards and A. L. Loomis, THIS JOURNAL, 49, 3086 (1927).

cloud of emulsion came off the walls of the tube slowly into the benzene layer only. There was little agitation of the interface, and the water layer remained clear until, after two minutes, when the benzene layer was extremely milky, a thin but gradually increasing haze of emulsion drifted down from the interface.

In dried test-tubes into which water was pipetted with great care to avoid wetting the upper part of the tube, and benzene then similarly added, no emulsification whatever took place unless the sound wave intensity was sufficient to agitate the interface considerably. Then emulsion formed at the wall-layer so produced, and was slowly driven through the liquid by radiation pressure. If drops of water were attached to the wall opposite the benzene layer they became milky and gradually emulsified completely. The converse was also true.

These results were verified with many immiscible liquids, a uniform indication being obtained with all. At low intensities of sound, emulsification evidently takes place almost wholly at the wall in contact with the dispersion medium when wetted with the liquid dispersed.

An attempt was made to study the action of sound waves on a benzene–water interface when confusing wall action was eliminated by damping out as far as possible vibrations in the glass. For this purpose a vessel was made consisting of a wide glass tube to the bottom of which was cemented a brass collar and a very thin brass membrane. Further lo damp vibrations in the glass it was wound with heavy layers of rubber bands immediately above and below the benzene–water interface. When radiated with sound care was taken to immerse only the brass collar in the oil transmitting sound waves from the vibrating crystal since, brass being a poor conductor of transverse waves, the greater part of the sound energy present in the tube must then enter the liquid through the metal membrane. Under these conditions no visible action took place at the interface, although with very high intensities of sound slow emulsifying action at the walls was noted. This is a further indication that the major part of the emulsifying process occurs at the wall.

The type of emulsion produced when mercury is dispersed in water demands another explanation, since mercury does not wet the glass tube. It has never been found possible, moreover, to cause the mutual solution of the mercury and water layers. In this case the action, if studied under varying conditions, takes place somewhat differently. It is dependent, in the first place, on the amount of mercury in the tube. If 1 cc. is present in a pyrex combustion tube with 10 cc. of water, emulsifying action proceeds rapidly. If 2 cc. of mercury is present it proceeds more slowly, and with 5 cc. of mercury it is almost completely arrested even with the highest sound wave intensity. This may safely be attributed to the damping action of the mercury on waves in the glass. When under the, best conditions for observation the emulsifying action may be seen to take place only in a small ring where the mercury, water and glass are in contact. Then white ribbons of emulsion are driven out slowly into the water from this circle. The action is accelerated by ammonium chloride, which is a pronounced emulsifying agent. Mercury withdrawn from sound action in water-wetted tubes and quickly strained through filter paper has an abnormally high water content, which it soon loses; it is therefore probable that water is emulsified in mercury, although the emulsion soon stratifies.

A picture of the mechanism of this emulsification may readily be formed on the basis of these results. It evidently is closely parallel to that described by Nordlund,[3] who obtained similar emulsions by bubbling water through a mercury layer.

2. Emulsification as a Measure of Sound Wave Intensity.—When this investigation was undertaken it was hoped that an absolute measure of local forces in the sound waves producing emulsification could be obtained. There remains, however, a certain usefulness for the emulsification process as a measure of relative sound intensities.

The following method makes this possible and gives, moreover, certain other valuable indications. Uniform test-tubes were coated internally with a mixture of celluloid and medicinal paraffin dissolved in acetone of such composition that, on the evaporation of the acetone and after drying for two hours at 70°, a coherent mixed film was formed which did not either peel or release paraffin on the introduction of water into the tube. By raying these tubes and measuring nephelometrically their turbidity, a standard of radiation intensity was obtained which was reproducible to about 20%.

The emulsification in these tubes, since it proceeded under almost optimal conditions, made possible the detection of exceedingly small intensities of sound. Only certain isolated spots on the glass surface were active in the process and ribbons of emulsified oil were shot from them across the tube. More emulsification took place at the top of the tube, which was open and hence relatively undamped, than at the bottom, which was necessarily immersed in oil.

3. The Emulsification of Glass in Water.—The intense emulsifying action at the wall of a glass vessel raises the question whether glass itself is emulsified on prolonged radiation. In more general investigations in progress with sound waves it is important to answer this and to ascertain with some precision the alteration of the properties of water if any occurs.

To this end pyrex tubes were washed with soap and water, heated with chromic acid and nitric acid and finally boiled repeatedly with distilled water. They were then filled by distillation without ebullition, being

---

[3] Nordlund, "Dissertation," Upsala, 1918.

washed with the water so distilled repeatedly until no further dust particles could be observed in the liquid. They were then sealed off without admission of air. In this way water was obtained showing only a faint uniform blue cone, due probably to the molecular scattering of water, with intense illumination and a black background.

One of these tubes was rayed with maximum intensity for sixty minutes. It showed a distinct increase in turbidity in an intense Tyndall beam, indicating that a small amount of glass had been torn from the sides, but the change in turbidity was not detectible with a precision nephelometer. By a dielectric loss method to be described elsewhere it was demonstrated that the electrolyte concentration was less than 10^{-6} N. The PH, as measured by bromthymol blue, was about 0.2 units more basic than that in an unrayed tube, but this was not considered significant in unbuffered water. Five cc. of the liquid from the rayed and from an unrayed tube evaporated on a watch glass showed that the former had a slightly greater non-xolatile content, but the difference was too small to be detectible on a precision analytical balance.

Since the result was clearly negative, except in so far as slight fragmentation of the sides of the tube was concerned, and since raying for an hour is a tedious matter, no further experiments of a similar nature were carried out.

These results make it appear unlikely that sound waves should in a liquid fracture small glass particles. This supposition was confirmed by experiment. Uniform glass particles which would pass an 80 to the inch but not pass a 100 to the inch sieve were selected, washed with chromic acid, and violently agitated many times with distilled water. Particles of this size were too small, if in low concentration, readily to undergo flocculation by the sound waves, and yet not small enough to be held in standing waves at the glass surface and thus suffer possible mechanical fracture. A standard weight of glass in water was rayed for unit intervals of time and an identical weight was simultaneously given violent mechanical agitation in another portion of water of the same volume. After raying, the water from the two was poured off and compared nephelometrically. The turbidity of both converged toward the same limit within error of measurement, indicating that, although patently more effective in detaching adhering smaller particles of glass, the sound waves were causing no more actual breakage of the larger particles than that which mechanical agitation produced.

Discussion

The observations recorded above indicate clearly that emulsification in a liquid takes place largely at the walls of the containing vessel when they are wetted with the liquid dispersed, This makes it improbable that compressional waves in the liquid produce the action; more probably the transverse waves in glass, noted by Wood and Loomis, are the effective agents. As described by these authors the transverse waves in a glass rod 0.1 mm. in thickness at a frequency of 300 K.C. have a wave length of about 6 mm., which gives an index to the general characteristics of similar waves in a test-tube of equal thickness. Their amplitude, as judged by their physical effects, must be far larger than that of the compressional waves in the same medium; measured under somewhat different conditions it was of the order of 6000 Å.

This conclusion makes it appear probable that many destructive phenomena, which have formerly been attributed to direct action of the sound waves in liquids, are, in fact, of a secondary nature. The rupture of blood cells, small unicellular organisms, and the like cannot now necessarily be supposed to take place in the liquid proper, but may evidently occur primarily in the neighborhood of the walls.[4] Any small body perceptibly adsorbed by the glass surface would, of course, be even more subject to this destructive action. Indeed, in all cases where sound is transmitted through a glass vessel into a liquid, transverse waves must be considered as a possible primary explanation for any effects observed. Action on dry explosives and liquid-in-air cloud production may safely be attributed to the same cause in most cases.

These data, furthermore, indicate clearly the method by which emulsification may be most effectively produced in any desired case. It is evidently unnecessary to have a liquid–liquid interface in the containing vessel except as an envelop for the dispersion medium. The same considerations, with obvious modification, apply equally to solid-liquid systems.

Finally, it follows that no measurements valuable for the estimation of the absolute radiation pressure in a liquid can be obtained from a study of emulsification. The effects of transverse wall waves must inevitably be confused with the effects of compressional waves in the liquid. Furthermore, even if, at high intensities, emulsification occurred at a plane liquid–liquid interface, it would not be amenable to quantitative treatment. The process of emulsification is, in such a case, a matter essentially of velocity and not of equilibrium: in order to be perceptible a definite amount of liquid must be dispersed in a given time. The radia-

---

[4] This statement must not be considered categorical. Turtle's blood is laked, although slowly, in a rubber bag in which transverse waves connot exist. Certain phenomena encountered in the capillary of a funnel gage [W. T. Richards, *Proc. Nat. Acad. Sci.*, 15,310 (1929)], where the sound energy is concentrated by reflection, indicate that fracture of a liquid–liquid surface may take place in the absence of transverse waves. The fracture of a gas–liquid interface by compressional waves in the liquid is evidently far easier. This is demonstrated strikingly at high sound intensities by the emergence from the capillary opening of a funnel gage of a fine spray, even when the capillary tube is tightly encased in rubber.

tion pressure of sound and the amount of energy necessary to convert a gram of substance from infinite radius to a small finite radius are both easy to estimate, but no specific mechanism can be formulated for the emulsification process and without this the two cannot be usefully equated. Since, moreover, the standing waves in liquids are shifting constantly both in intensity and in position, it seems certain that, even if it occurred, emulsification would under these conditions lead to no useful conclusions.

Summary

It has been demonstrated that emulsions produced by sound waves are due largely to action at the walls of the vessel. A method has been devised whereby the process of emulsification may be used as a fairly reliable measure of relative intensities of sound. An argument is advanced which makes it appear unlikely that absolute radiation pressures can be calculated from any similar process. It has been demonstrated that the walls of a glass vessel are slightly emulsified and that small uniform glass particles in liquids are not fractured by intense sound waves.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. III. THE ANALYSIS OF NICKELOUS BROMIDE

BY GREGORY PAUL BAXTER AND SABURO ISHIMARU

RECEIVED FEBRUARY 18, 1929 PUBLISHED JUNE 5, 1929

In two recent investigations comparisons of terrestrial and meteoric nickel have been made by the quantitative determination of nickel in nickelous oxide[1] and of chlorine in nickelous chloride.[2] In both series of experiments the meteoric nickel was obtained from the same source, the Cumpas meteorite found in 1903, near Cumpas, Sonora, Mexico. In neither case could any difference be detected between the atomic weights of terrestrial and meteoric nickel larger than the error of the experiments. Since the origin of any meteorite must necessarily be largely a matter of conjecture, the possibility of a difference in the isotopic composition of nickel from different meteorites, although remote, is not negligible. Therefore, the availability of a considerable quantity of meteoric nickel from another source has led us to a new comparison of this material with that of terrestrial origin. In order to vary the method somewhat from those outlined above and in order to take advantage of the very great suitability of silver bromide for precision work, in this case nickelous

---

[1] Baxter and Parsons, THIS JOURNAL, 43,507 (1921).

[2] Baxter and Hilton, *ibid.*, 45,694 (1923).

bromide was selected for analysis. As before, we have been unable to establish any difference between terrestrial and extra terrestrial material.

Purification of Materials

The preparation of reagents followed lines already proved to be adequate in numerous earlier investigations. Water, nitric acid, hydrochloric acid, formic acid, ammonium carbonate and ammonia were purified by distillation. Silver was especially important as being the standard of comparison. The processes employed were double precipitation of the chloride followed in each case by reduction with sugar solution made alkaline with electrolytically purified sodium hydroxide, fusion of the metal on a lime boat in a blast flame, solution in nitric acid and repeated crystallization of silver nitrate, precipitation of the metal with ammonium formate, fusion on pure lime in an electrically heated muffle, electrolytic transport through a concentrated silver nitrate solution made from the same silver, fusion on pure lime in an atmosphere of pure dry electrolytic hydrogen, etching with nitric acid and drying in a vacuum at 500°.[3]

Pure lime was made from calcium nitrate which had been recrystallized until free from iron and then precipitated as carbonate. To prepare receptacles for the fusion of silver, the carbonate was ignited and a mixture of the product with a small proportion of nitrate was used to line either porcelain crucibles or porcelain boats.

Bromine was first distilled from aqueous potassium bromide to remove the bulk of the chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate and the remaining three-fourths of the bromine was distilled from solution in the potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate and the potassium bromide was fused in a platinum dish with enough recrystallized potassium permanganate to oxidize all organic matter. In order to obtain bromine, the purified potassium bromide was dissolved in a solution of pure sulfuric acid and the potassium sulfate which separated was removed. The excess of permanganate in the bromide caused a small quantity of bromine, to be liberated. This bromine was removed by distillation, since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. After separation from the aqueous layer, the pure bromine was redistilled. In all the above operations cork and rubber' were rigidly excluded from the apparatus.

Hydrogen bromide was prepared from the bromine by catalytic synthesis

---

[3] See especially Richards and Wells, *Pub. Car. Inst.*, No. 28, p. 16 (1905); Baxter, THIS JOURNAL, 44,591 (1922).

with hydrogen. Electrolytic hydrogen dried by fused potassium hydroxide was charged with bromine at about 44° and the mixture passed over hot platinized asbestos in a hard glass tube. To prepare an aqueous solution the product was collected in water and the solution distilled through a quartz condenser with rejection of the extreme portions. To obtain the pure, dry gas a slight excess of bromine was used and the product freed from bromine by being passed through an aqueous solution containing pure ferrous bromide. The comparatively small amount of water which evaporated from the saturated hydrogen bromide solution was removed by fused calcium bromide since phosphorus pentoxide reacts with the gas. Calcium bromide leaves 0.2 mg. of water per liter of gas. There was no evidence, however, that this small quantity of moisture reacted with nickelous bromide in the presence of a high concentration of hydrogen bromide.

Nitrogen was prepared from air with an excess of ammonia by the Wanklyn catalytic process and the hydrogen produced catalytically was oxidized by hot copper oxide. After drying the gas thoroughly, oxygen liberated from the cupric oxide was removed by hot nickel.

Air was passed over aqueous silver nitrate and potassium hydroxide, concentrated sulfuric acid and phosphorus pentoxide and through a sintered glass filter.

All the apparatus for purifying gases was constructed of glass with fused or well ground joints. No lubricant whatever was used on the ground joints since past experience has shown that organic greases evaporate sufficiently to introduce carbonaceous residues into substances otherwise free from organic material, while inorganic lubricants are likely to carry moisture to the interior.

Purified terrestrial nickel chloride and metal remaining from earlier work were converted to nitrate by treatment with nitric acid, and nickel ammonia nitrate was produced by saturating the solution with distilled ammonia. This salt was recrystallized four times by solution in hot water kept saturated with ammonia, followed by cooling. Centrifugal separation of crystals from mother liquor was carried out in platinum Gooch crucibles. From the nickel ammonia nitrate the hydroxide was prepared by hydrolysis. The salt was treated with a considerable amount of water in platinum dishes and kept at boiling temperature until ammonia ceased to be evolved. The precipitate was washed, dried and ignited. The product was then dissolved in nitric acid and the nitrate crystallized three times from concentrated nitric acid. Decomposition of the nitrate at a high temperature in a platinum boat yielded the oxide a second time. This was dissolved in pure aqueous hydrogen bromide, in a quartz vessel to avoid the action of bromine liberated by the higher oxides of nickel. The bromide was then crystallized four times in platinum vessels with centrifugal drainage.

The meteoric nickel was obtained in the course of the extraction of cobalt for the earlier investigation. The source was a meteorite probably found in the western part of the United States, and possibly was a portion of the Cañon Diablo meteorite. Professor Emeritus J. E. Wolff, of Harvard University, very generously donated this material. Originally about 7 kilograms of the meteorite was dissolved in nitric acid and the iron largely separated by crystallization as ferric nitrate. Nearly all the remaining iron was removed by precipitating the sulfides and extracting with dilute hydrochloric acid. The cobalt was then separated by treatment with a large excess of potassium nitrite in the presence of acetate. The remaining salts were converted to chlorides by evaporation with hydrochloric acid and those metals forming less soluble sulfides were removed by fractionation with hydrogen sulfide in slightly acid solution. Conversion of the salts to nitrates by evaporation with an excess of nitric acid was followed by precipitation of the iron with a large excess of ammonia in dilute solution. After evaporation of the solution, nickel ammonia nitrate was prepared as with the terrestrial material. The subsequent steps in the preparation of nickelous bromide were identical with those outlined above.

To prepare anhydrous nickelous bromide for analysis the hydrated salt was first partially dehydrated over fused potassium hydroxide at room temperature. The residual water was then removed by heating the salt, contained in a quartz boat, in a quartz tube through which a mixture of nitrogen and hydrogen bromide was passed at about **360"**. Sublimation of the anhydrous material from the boat to the tube in the same atmosphere then followed and the product was twice resublimed to adjacent portions of the tube. As in the case of nickelous and cobaltous chlorides which had been similarly prepared, a slight siliceous residue remained, diminishing with each sublimation. In a second triple sublimation no evidence of silica could be detected. The final product was preserved over fused potassium hydroxide for analysis.

Before being weighed the dehydrated bromide was again heated to the sublimation point in a current of dry nitrogen and hydrogen bromide. The salt, contained in a weighed platinum boat, was placed in a transparent quartz tube which formed part of a Richards and Parker[4] bottling apparatus. After the air had been displaced the tube was electrically heated at gradually increasing temperatures until finally the bromide began to sublime. After the tube had been allowed to cool, the hydrogen bromide was displaced by dry nitrogen and this in turn by dry air before the boat was transferred to the weighing bottle in which it had been originally weighed. A second weighing of the bottle and boat followed.

The boat and contents were next covered with about **1000** ml. of pure water in a precipitating flask, and allowed to stand for several days until

---

[4] Richards and Parker, *Proc Am. Acad.*, **32,** 59 (1896).

solution was complete. There was never the slightest evidence of insoluble matter. The boat was then carefully removed and at the same time was thoroughly rinsed. Pure silver nearly equivalent to the bromide was weighed out, dissolved in nitric acid and diluted to approximately 0.1 N concentration. The silver solution was then added to the bromide solution in small portions with frequent shaking and the flask was allowed to stand at room temperature for some days with occasional agitation. The clear supernatant solution was next tested in a nephelometer for excess of bromide or silver, and the estimated deficiency of either was added in the form of 0.01 N solution. The solution was then shaken, allowed to clarify and tested as before and the process was repeated until exactly equivalent quantities of silver and bromide had been used. A period of six to eight weeks in every case elapsed between the precipitation and the final adjustment of equilibrium, since long experience has shown that this is necessary for the leaching out of material initially occluded by the precipitate.

In all but two analyses, after the end-point of the comparison had been reached, an excess of silver nitrate (from 0.002 to 0.02 g.) was added and the analyses were allowed to stand for some time longer. Then after the silver bromide had been washed many times with pure water it was collected on a weighed platinum sponge Gooch crucible and dried in an electrically heated porcelain air-bath at a temperature not far from 400° before being weighed. In Analyses 10, 11 and 13, the main bulk of the precipitate was transferred to a porcelain crucible and the loss on fusion, presumably due to retained moisture, was determined.

In Analysis 9 the silver bromide was accidentally fused in the Gooch crucible during the initial drying. Since no apparent deterioration of the bromide resulted, in Analysis 12 the bromide was first dried at 370° and weighed and then was fused for a short time in the Gooch crucible. A loss in weight of 0.12 mg. resulted. Three repetitions of the fusion for periods of two, two and four hours resulted in changes in weight of -0.05, $+0.03$, and -0.11 mg. In Analysis 14, also, the silver bromide was once fused in the Gooch crucible after having been dried at 360° and weighed. These experiments so far as they go indicate that a short period of fusion in the platinum sponge crucible introduces little danger from decomposition of the silver bromide, although prolonged fusion is doubtless objectionable. This method has the great advantage of avoiding the transfer of the dried precipitate to a porcelain crucible for the fusion. Further experiments in this direction are obviously desirable. The small proportion of moisture found in these precipitates, 0.0005%, is in accordance with the observation by Hönigschmid and Birckenbach[5] that silver chloride dried at 300° is nearly if not quite anhydrous.

[5] Honigschmid and Birckenbach, *Z. anorg. allgem. Chem.*, **163**, 332 *(1927)*.

Slight corrections were .applied to the weight of silver bromide for solubility in the mother liquors and wash waters,[6] for silver bromide found in an ammoniacal solution with which the precipitating flask was finally rinsed, and for bromide introduced during the nephelometric comparison of the nickelous bromide with silver.

All objects were weighed by substitution for similar counterpoises. Weights were standardized to hundredths of a milligram by the Richards substitution method.[7] Vacuum corrections were applied on the basis of the air density observed at the time of weighing, and the following densities: weights, 8.3; $NiBr_2$, 4.64; AgBr, 6.47; Ag, 10.49.

TABLE I

THE ATOMIC WEIGHT OF NICKEL

Ag = 107.880 Br = 79.916

$NiBr_2:2Ag$, Series I

		Wt. of $NiBr_2$ in vac.	Wt. of Ag in vac.	Wt. of Ag added	Corr. wt. of Ag in vac.	Ratio $NiBr_2$: 2Ag	Atomic weight of Ni
1	T	4.97931	4.91632	−0.00011	4.91621	1.012835	58.697
2	T	5.33870	5.27128	− .00027	5.27101	1.012842	58.699
3	T	7.91596	7.81825	− .00245	7.81580	1.012815	58.693
4	T	4.63096	4.57239	+ .00003	4.57242	1.012803	58.690
5	T	5.35138	5.28445	+ .00097	5.28348	1.012851	58.701
					Average	1.012829	58.696
				Series II			
6	M	6.31054	6.22997	+0.00071	6.23068	1.012817	58.693
7	M	5.66561	5.59408	+ .00011	5.59419	1.012767	58.683
8	M	6.08659	6.00959	− .00011	6.00948	1.012831	58.696
					Average	1,012805	58.691
				Average of Series I and II			58.694

$NiBr_2:2AgBr$, Series III

		Wt. of $NiBr_2$ in vac.	Wt. of AgBr in vac.	Loss on fusion	Dissolved AgBr	Corr. wt. of AgBr	Ratio $NiBr_2$:-2AgBr	Atomic weight of Ni
9	T	4.97931	8.55738		0.00049	8.55787	0.581840	58.702
10	T	7.91596	13.60528	0.00007	.00012	13.60533	.581828	58.698
11	T	4.63096	7.95987	.00000	.00008	7.95995	.581783	58.681
						Average	.581817	58.694
				Series IV				
12	M	6.31054	10.84634	0.00012	0.00006	10.84628	0.581816	58.693
13	M	5.66561	9.73791	.00002	.00008	9.73797	.581806	58.690
14	M	6.08659	10.46106	.00006	.00006	10.46106	.581833	58.700
						Average	.581818	58.694
					Average of Series III and IV			58.694
					Average of Series I and III			58.695
					Average of Series II and IV			58.693
					Average of all Series			58.694

---

[6] Calculated on the basis of a solubility of silver bromide in water of 0.1 mg. per liter.

[7] Richards, THIS JOURNAL, 22,144 (1900).

Within the experimental error the terrestrial and meteoric samples are identical in isotopic composition. The combined average result, 58.694, would be raised only 0.002 unit by the omission of the two most discordant determinations, Analyses 7 and 11.

Modern determinations of the atomic weight of nickel are given in chronological order in the following table.

Richards and Cushman	$NiBr_2:2Ag$	58.680	**Baxter and Parsons**	$NiO:Ni$	58.702
	$NiBr_2:2AgBr$	58.683	**Baxter and Hilton**	$NiCl_2:2Ag$	58.6998
				$NiCl_2:2AgCl$	58.701[8]
	$NiBr_2:Ni$	58.682	**Baxter and Ishimaru**	$NiBr_2:2Ag$	58.695
				$NiBr_2:2AgBr$	58.693
	Average	58.682		Average	58.698

As has been pointed out before, the material analyzed by Richards and Cushman was not ideal for the purpose since it contained impurity extracted from the porcelain tube during sublimation. The average of the more modern values is almost 0.02 unit higher than the older one of Richards and Cushman and probably is nearer the truth.

During a temporary absence of the senior author, for a portion of the time, oversight of this work was undertaken by the late Professor T. W. Richards. We gratefully acknowledge our indebtedness for his kind advice.

Summary

1. Nickel extracted from a new meteorite has been found to have the same isotopic composition as terrestrial nickel.
2. The atomic weight of nickel has been found to be 58.694.
3. The average of the most recent determinations of this constant is 58.697.

CAMBRIDGE, MASSACHUSETTS

---

[8] Calculated with the value 35.457 for chlorine.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. IV. THE DEPENDENCE OF MOLAR REFRACTION UPON CONCENTRATION IN MIXTURES

BY C. P. SMYTH, E. W. ENGEL AND E. BRIGHT WILSON, JR.

RECEIVED FEBRUARY 23, 1929 PUBLISHED JUNE 5, 1929

In considering the dependence of the polarization of a binary mixture upon composition, it has been customary to attribute all deviations from a linear relation to variation in the polarization due to orientation of the dipoles. The molar polarization, P_{12}, of a mixture of two liquids 1 and 2 is represented by the expression

$$P_{12} = c_1P_1 + c_2P_2 = P_1 + c_2(P_2 - P_1)$$

in which P_1 and P_2 are the polarizations and c_1 and c_2 the mole fractions of Components 1 and 2, respectively. From this it follows that P_{12} is a linear function of c_2 if P_1 and P_2 are constant. The polarization of a pure substance is regarded as the sum of three quantities, the polarization P_E caused by electronic shifts induced in the molecules, the small polarization P_A attributed mainly to shifts of atoms or radicals induced in the molecules, and P_M caused by orientation of the molecular dipoles. P_A is difficult to determine accurately, but is usually small in comparison with P_E and sometimes very small in comparison with P_M. The possible variation with concentration of P_A for a substance in solution need not, therefore, be considered as a serious factor in our present methods of obtaining polarization. The assumption of the independence of P_E of concentration has appeared warranted by the approximate constancy found in a number of mixtures for the Lorentz–Lorenz expression for the molar refraction,[1] which is equivalent to P_E, that is, $P_E = (n^2 - 1)/(n^2 + 2)M/d$, in which n is the refractive index, M is the molecular weight and d is the density. The electronic polarization of a mixture of two components 1 and 2 is

$$P_{E,1,2} = \frac{n^2 - 1}{n^2 + 2} \times \frac{c_1M_1 + c_2M_2}{d} = P_{E,1} + c_2(P_{E,2} - P_{E,1})$$

in which M_1 and M_2 are the molecular weights of 1 and 2 and $P_{E,1}$ and $P_{E,2}$ are the electronic polarizations or molar refractions of the two components.[2] Not only the approximate constancy found for the molar refractions in a number of mixtures but also the additivity of the refractions of radicals give ground for the belief that $P_{E,1}$ and $P_{E,2}$ are usually approximately independent of c_2. However, the refraction calculated

---

[1] See Smiles, "The Relations between Chemical Constitution and Some Physical Properties," Longmans, Green and Co., London, 1910, p. 244.

[2] Cf. Debye, "Handbuch der Radiologie" (Marx), Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1925, Vol. VI, p. 619.

for an isolated ion has been found to be different from that possessed by the ion when attached to other ions because the forces acting on the outer electrons are different.[3] It would appear possible, therefore, that the occurrence of pronounced molecular association in a liquid might affect the forces acting on the outer electrons of the molecules. Change in the degree of association of the molecules brought about by change of temperature or change in the concentration of a mixture might alter the forces acting upon some of the outer electrons and thus alter the polarization. It has been shown for a number of substances that the molar refraction does not change much with temperature or even with change of state, but it has seemed desirable to use a series of refractive index measurements carried out upon fifteen pairs of liquids to examine further the constancy of $P_{E,1}$ and $P_{E,2}$. Unfortunately, the densities are not available for a number of these mixtures, but all the refractive indices are, nevertheless, reported. The liquids used were carefully purified but, as the same materials were used for vapor pressure measurements, the methods of purification and the criteria of purity are given elsewhere.[4] The excellent agreement of the indices of the pure components with the values contained in the literature is evidence of their purity.

The indices of refraction for the sodium D line were measured with a Pulfrich refractometer, a temperature of 20° constant within 0.01" being obtained by a flow of water from carefully adjusted thermostats. The probable error in a value of the index was 0.00007. The results are given in Table I, in which the first column under each pair of substances gives the mole fraction of one component and the second the refractive index. In order to show the deviation of the refractive indices from a linear dependence upon composition, the third column gives the composition calculated from the observed refractive index on the assumption that the latter is a linear function of composition. For example, a refractive index half way between the values for the pure components of a mixture would give a calculated mole fraction of 0.5000. The difference between the known value of the mole fraction and that calculated in this manner is given in the fourth column as a measure of the departure from a linear relation between refractive index and composition.

The densities of the mixtures of several of these pairs of substances have been determined by Mr. W. N. Stoops and Mr. H. E. Rogers and will be published in another connection. The values of the refractive indices for the concentrations at which the densities were determined were obtained by interpolation. Additional refractive indices for the sodium D line and densities were selected from the measurements of Williams and Krchma, who determined these quantities at 25° for a few mixtures of a

---

[3] Fajans and Joos, *Z. Physik*, **23**, 1 (1924); Smyth, *Phil. Mag.*, **50**, 361 (1925).

[4] Smyth and Engel, THIS JOURNAL, **51** (1929).

TABLE I

REFRACTIVE INDICES (n_D) OF BINARY MIXTURES AT 20°

Carbon Tetrachloride–Heptane

M. f., C_7H_{16}	n_D	M. f , calcd.	Diff.
0	1.46026	...	...
0.0335	1.45643	0.0528	0.0187
.0705	1.45221	.1109	.0404
.1422	1.44484	.2124	.0702
.2181	1.43759	.3123	.0942
.2989	1.43056	.4091	.1102
.3430	1.42700	.4582	.1152
.3825	1.42382	.5020	.1195
.4383	1.41962	.5598	.1215
.4811	1.41656	.6027	.1216
.5883	1.40945	.7000	.1117
.7071	1.40243	.7967	.0896
.8348	1.39553	.8916	.0568
.9072	1.39201	.9402	.0330
1.0000	1.38767	...	...

Heptane–Ethyl Bromide

M. f., C_2H_5Br			
0	1.38770	...	...
0.1251	1 38940	0.0469	0.0782
.2227	1.39095	.0898	.1329
.3019	1.39258	.1345	.1674
.3162	1.39289	.1430	.1732
.4724	1.39680	.2508	.2216
.5136	1.39807	.2858	.2278
.5724	1,40004	.3401	.2323
.6121	1.40142	.3782	.2339
.6526	1.40310	.4245	.2281
.6886	1.40454	.4642	.2244
.7308	1.40646	.5171	.2137
.7740	1.40854	.5744	.1996
.7998	1.41004	.6158	.1840
.8453	1.41262	.6869	.1584
.8646	1.41377	.7186	.1460
.9064	1.41662	.7971	.1093
.9439	1.41932	.8716	.0723
1.0000	1.42398	...	...

Heptane–Butyl Bromide

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0	1.43984	...	...
0.0496	1.43612	0.0713	0.0217
.1020	1.43251	.1405	.0385
.1471	1.42950	.1982	.0511
.2299	1.42410	.3017	.0718
.3222	1.41870	.4052	.0830
.3667	1.41600	.4570	.0903
.4167	1.41321	.5104	.0937
0.5095	1.40836	0.6034	0.0939
.6136	1.40333	.6998	.0862
.7235	1.39834	.7955	,0720
.7884	1.39570	.8461	.0577
.8427	1.39347	.8888	.0461
.9038	1.39114	.9335	.0297
1.0000	1.38767	...	...

Heptane–Ethyl Iodide

M. f., C_7H_{16}			
0	1.51330	...	...
0.0596	1.49882	0.1153	0.0557
.1297	1.48358	.2366	.1069
.2018	1.47007	.3442	.1424
.2795	1.45716	.4470	.1675
.3219	1.45076	.4979	.1760
.3632	1.44494	.5443	.1811
.4138	1.43821	.5978	.1840
.4612	1.43247	.6435	.1823
.5723	1.42042	.7395	.1672
.6903	1.40934	.8277	.1374
.8407	1.39768	.9205	.0798
1.0000	1.38770	...	...

Heptane–Ethyl Alcohol

M. f., C_7H_{16}			
0	1.36130	...	...
0.0207	1.36221	0.0345	0.0138
.0506	1.36355	.00853	.0347
.0723	1.36448	.1206	.0483
.0985	1.36566	.1653	.0668
.1554	1.36805	.2560	.1006
.2184	1.37044	.3466	.1282
.2537	1.37161	.3910	.1373
.2945	1.37292	.4407	.1462
.3369	1.37426	.4915	.1546
.3816	1.37540	,5347	.1531
.4946	1.37830	.6447	.1501
.6150	1.38091	.7437	.1287
.6964	1.38246	.8024	.1060
.7901	1.38409	.8636	.0735
.8878	1.38573	.9264	.0386
1.0000	1.38767	...	...

Hexane–Heptane

M. f., C_7H_{16}			
0	1.37508	...	...
0.1743	1.37748	0.1902	0.0159

TABLE I (*Continued*)

Hexane–Heptane

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0.2216	1.37814	0.2425	0.0209
.4029	1.38051	.4303	.0274
.4708	1.38137	.4984	.0276
.5705	1.38261	.5967	.0261
.6103	1.38309	.6340	.0237
.6709	1.38376	.6878	.0169
.7176	1.38434	.7337	.0161
.7706	1.38492	.7797	.0091
.8748	1.38616	.8780	.0033
1.0000	1.38770	...	...

Heptane–Butyl Chloride

M. f., C_7H_{16}			
0	1.40173	...	...
0.0449	1.40059	0.0811	0.0362
.0669	1.40012	.1145	.0476
.1468	1.39842	.2354	.0886
.2276	1.39678	.3521	.1245
.3198	1.39522	.4630	.1432
.3598	1.39456	.5100	.1502
.4066	1.39383	.5619	.1553
.4540	1.39314	.6109	.1569
.5008	1.39252	.6550	.1542
,6159	1.39105	.7596	.1437
.7202	1.38992	.8400	.1198
.9134	1.38823	.9602	.0468
1.0000	1.38767	...	...

Heptane–Heptyl Bromide

M. f., $C_7H_{15}Br$			
0	1.38770	...	...
0.1022	1.39455	0.1094	0.0072
.1919	1.40043	.2033	.0114
.2715	1.40558	.2856	.0141
.3674	1.41183	.3854	.0180
.4194	1.41522	.4395	.0201
.4725	1.41862	.4939	.0214
.5151	1.42122	.5354	.0203
.6702	1.43087	.6895	.0193
,7713	1.43700	.7874	.0161
.8840	1.44354	.8919	.0079
1.0000	1.45031	...	...

Heptane–Butyl Alcohol

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0	1.39942	...	...
0.0327	1.39883	0.0502	0.0175
,1336	1.39707	.2000	.0664
.2104	1.39579	.3089	.0985
0.2867	1.39448	0.4204	0.1337
,3321	1.39377	.4809	.1488
.3767	1.39313	.5353	.1586
.4249	1.39252	.5872	.1623
.5795	1.39069	.7430	.1635
.6989	1.38945	.8485	.1496
.8327	1.38833	.9438	.1111
.9097	1.38788	.9821	.0724
1.0000	1.38767	...	...

Ethyl Bromide–Ethyl Iodide

M. f., C_2H_5I			
0	1.42408	...	...
0.1937	1.44143	0.1945	0.0008
.2901	1.45016	.2923	.0022
.3151	1.45247	.3182	.0031
.3824	1.45866	.3876	.0052
.4280	1.46264	.4322	.0042
.4732	1.46671	.4778	.0046
.5148	1.47036	.5187	.0039
.5741	1.47567	.5782	.0041
.6114	1.47899	.6154	.0040
.6750	1.48471	.6796	.0046
.7640	1.49258	.7678	.0038
.8817	1.50302	.8848	.0031
1.0000	1.51330	...	...

Butyl Chloride–Butyl Bromide

M. f., C_4H_9Br			
0	1.40173	...	...
0.0444	1.40353	0.0472	0.0028
.0832	1.40518	.0905	.0073
.1903	1.40935	.1999	.0096
.2878	1.41309	.2981	.0103
.3888	1.41703	.4015	.0127
.4333	1.41874	.4463	.0130
.4842	1.42062	.4957	.0115
.5307	1.42233	.5405	.0098
.5791	1.42430	.5922	.0131
.6816	1.42826	.6962	.0146
.7798	1.43187	.7909	.0111
.8844	1.43585	.8953	.0109
.9397	1.43792	.9496	.0099
1.0000	1.43984	...	...

Carbon Tetrachloride–Butyl Alcohol

M. f., C_4H_9OH			
0	1.46026	...	...
0.0555	1.45677	0.0574	0.0019

TABLE I *(Concluded)*

Carbon Tetrachloride–Butyl Alcohol

M. f , C_4H_9OH	n_D	M. f., calcd.	Diff
0.1196	1.45307	0.1182	0 0014
.1686	1.45017	.1659	.0027
.2255	1.44687	.2201	.0054
.3240	1.44125	.3125	.0115
.4243	1.43532	.4099	.0144
.4742	1.43251	.4561	.0181
.5214	1.42980	.5007	.0207
.5707	1.42690	.5483	.0224
.6197	1.42390	.5976	.0221
.7154	1.41830	.6897	.0257
.8095	1.41212	.7913	.0182
.8598	1.40886	.8448	.0150
.9117	1.40540	.9017	.0100
.9505	1.40280	.9445	.0060
1.0000	1.39942	...	...

Butyl Bromide–Butyl Alcohol

M. f., C_4H_9Br			
0	1.39942	...	...
0.0506	1.40177	0.0580	0.0072
.1394	1.40570	.1550	.0156
.1711	1.40698	.1866	.0155
.2673	1.41124	.2917	.0244
.3580	1.41500	.3845	.0265
.4155	1.41690	.4314	.0259
.4520	1.41870	.4758	.0238
.4780	1 41970	.5005	.0225
.5484	1 42240	.5671	.0187
.7622	1.43065	.7707	.0085
.8188	1.43291	.8265	.0077
1.0000	1.43994	...	...

Ethyl Bromide–Ethyl Alcohnl

M. f., C_2H_5OH	n_D	M. f., calc.	Diff.
0	1.42403	...	...
0.0729	1.41992	0.0657	0.0072
.1220	1.41717	.1097	.0123
.1646	1.41477	.1481	.0165
.2427	1.41027	.2201	.0226
.2749	1.40830	.2516	.0233
.3765	1.40256	.3435	.0330
.4100	1.40058	.3751	.0349
.4780	1.39646	.4407	.0373
.5337	1.39312	.4945	.0392
.5949	1.38935	.5548	.0401
.6538	1.38559	.6149	.0389
.7218	1.38118	.6850	.0368
.7767	1.37748	.7447	.0320
.8166	1.37475	.7884	.0282
.8930	1.36934	.8749	.0181
.9382	1.36603	.9279	.0103
1.0000	1.36152	...	...

Ethyl Iodide–Ethyl Alcohol

M. f., C_2H_5OH			
0	1.51330	...	...
0.1393	1.49552	0.1171	0.0222
.2594	1.47967	.2216	.0378
.3681	1.46472	.3201	.0480
.4759	1.44906	.4232	.0527
.5156	1.44314	.4622	.0534
.5268	1.44153	.4729	.0539
.5744	1.43408	.5219	.0525
.6248	1.42614	.5743	.0505
.6636	1.41992	.6152	.0484
.7517	1.40528	.7116	.0401
.8439	1.38950	.8157	.0282
.9345	1.37329	.9225	.0120
1.0000	1.36152	...	...

considerable number of pairs of substances.[5] Some of the latter data were eliminated because of apparent small discrepancies, while a few pairs were omitted as being of less interest than the others. Table II gives the results of the calculations from the data in Table I combined with the densities mentioned. The first column gives the mole fraction of one of the two components, the second column gives the value of $(n^2 - 1)/(n^2 + 2)(c_1M_1 + c_2M_2)/d$, which is the observed $P_{E,1,2}$, the third column gives the value of $c_1P_{E,1} + c_2P_{E,2} = P_{E,1} + c_2(P_{E,2} - P_{E,1})$, where $P_{E,1}$ and $P_{E,2}$ are taken as the values of the pure components, and the fourth column gives the difference between the observed and calculated. As the

---

[5] Williams and Krchma, THIS JOURNAL, 49, 1678, 2408 (1927).

probable error in the density determinations was 0.0002 and in the refractive indices 0.00007, the probable error in the observed value of $P_{E,1,2}$ should usually be about 0.014. The results calculated from the data of Williams and Krchma are shown in Table III, in which the error is probably somewhat greater than in Table II, although the less certain results have been eliminated.

TABLE II

MOLAR REFRACTIONS (D LINE) AT 20°

Heptane–Butyl Chloride

M. f., C_4H_9Cl	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	34.530	(34.530)	...
0.0242	34.363	34.310	0.053
.0653	33.943	33.938	.005
.0889	33.737	33.724	.013
.1562	33.116	33.113	.003
.2617	32.190	32.157	.033
.5619	29.463	29.434	.029
.8623	26.743	26.710	.033
1.0000	25.461	(25.461)	...

Heptane–Butyl Bromide

M. f., C_4H_9Br	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	34.527	(34.527)	.....
0.0456	34.235	34.244	−0.009
.0930	33.939	33.951	− .012
.1409	33.643	33.654	− .011
.2579	32.924	32.929	− .005
.4154	31.923	31.953	− .030
.5958	30.816	30.835	− .019
.8413	29.299	29.313	− .014
1.0000	28.330	(28.330)	.....

Heptane–Ethyl Iodide

M. f., C_2H_5I			
0	34.530	(34.530)	.....
0.0328	34.191	34.195	−0.004
.0843	33.664	33.669	− .005
.1889	32.617	32.600	+ .017
.4130	30.271	30.310	− .039
.6155	28.181	28.241	− .060
.8035	26.291	26.320	− .029
1.0000	24.312	(24.312)	.....

Heptane–Heptyl Bromide

M. f., C_4H_9Br			
0	34.530	(34.530)	.....
.0488	34.901	34.907	−0.006
.0889	35.212	35.216	− .004
.1626	35.806	35.785	.021
.3330	37.124	37.100	.024
.5327	38.644	38.642	.002
1.0000	42.249	(42.249)	.....

Heptane–Ethyl Alcohol

M. f., C_2H_5OH			
0	34.527	(34.527)	..
0.0312	34.167	34.141	0.026
.0525	33.892	33.877	.015
.0805	33.544	33.530	.014
.1043	33.256	33.237	.019
.1383	32.848	32.815	.033
.2655	31.263	31.240	.023
.4451	29.025	29.017	.008
.6152	26.917	26.912	.005
.8042	24.591	24.572	.019
1.0000	22.148	(22.148)	..

Heptane–Butyl Alcohol

M. f., C_4H_9OH			
0	34.527	(34.527)	.....
0.0256	33.991	33.974	0.017
.4252	25.322	25.333	− .011
.6142	21.222	21.246	− .024
.8300	16.604	16.581	.023
.9260	14.504	14.505	− .001
1.0000	12.905	(12.905)	.....

The average deviation of the individual differences in Table II from their arithmetical mean is of the same order of magnitude as the mean itself and as the probable error estimated for the individual values of $P_{E,1,2}$ (obs.). Consequently, it may be concluded that the difference,

TABLE III

MOLAR REFRACTIONS (D LINE) AT 25°

Carbon Tetrachloride–Benzene

M. f., CCl_4	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	26.194	(26.194)	..
0.25	26.290	26.263	0.027
.50	26.380	26.332	.048
.75	26.456	26.401	.055
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Ethyl Ether

M. f., CCl_4	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	22.513	(22.513)	..
0.25	23.558	23.502	0.056
.50	24.526	24.491	.035
.75	25.529	25.480	.049
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Methyl Acetate

M. f., CCl_4			
0	17.598	(17.598)	..
0.25	19.826	19.815	0.011
.50	22.049	22.033	.016
.75	24.241	24.250	−.009
.90	25.680	25.582	.098
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Acetone

M. f., CCl_4			
0	16.186	(16.186)	..
0.60	22.371	22.356	0.015
.70	23.416	23.384	.032
.75	23.901	23.898	.003
.90	25.496	25.441	.055
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Ethyl Alcohol

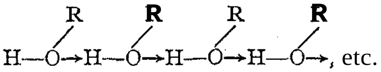
M. f., CCl_4			
0	12.893	(12.893)	..
0.50	19.725	19.681	0.044
.60	21.092	21.039	.053
.75	23.114	23.075	.039
.90	25.137	25.111	.026
1.00	26.469	(26.469)	..

Carbon Tetrachloride–*Iso*-amyl Alcohol

M. f., CCl_4			
0	26.754	(26.754)	..
0.75	26.574	26.540	0.034
.90	26.498	26.497	.001
1.00	26.469	(26.469)	..

less than 0.1%, between the observed and calculated values of $P_{E,1,2}$ is no larger than the experimental error. In other words, $P_{E,1}$ and $P_{E,2}$ are constant as far as can be measured throughout the mixtures, which means that in these liquids the contribution to the polarization of the electronic shifts induced in a molecule is practically independent of the surrounding molecules. The differences are about one-tenth as large as those found by Falk[6] between the molar refractions of several substances at 20 and at 80°.

These results have an interesting bearing upon the problem of molecular association. Sidgwick[7] states that "the great majority of associated substances contain a hydroxyl group," polymerization arising through the hydroxyl "hydrogen acting as acceptor and the oxygen as donor," that is, the hydrogen of one hydroxyl group becomes attached to the oxygen of the hydroxyl of another molecule and, as a result, shares electrons with both oxygens. Alcohol molecules would associate thus



$$H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}, \text{ etc.}$$

---

[6] Falk, THIS JOURNAL, 31, 86, 807 (1909); *Z. physik. Chem.*, 82, 504 (1913).

[7] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, England, 1927, p. 134.

It has been shown that an oxygen atom with a completed octet of electrons to which two hydrogen nuclei are attached to form a water molecule has a refraction of 3.76. When one of the linkages to hydrogen is replaced by a linkage to carbon, the refraction is reduced to 3.23, and when both hydrogen linkages are replaced by carbon linkages the refraction is reduced to 2.85.[3] Fajans and Joos[3] have calculated the following refractions: O^{--}, 7; OH^-, 5.10; OH_2, 3.75; OH_3^+, 3.04. Evidently, the attachment of a hydrogen nucleus to oxygen brings about a considerable reduction in the refraction. A somewhat smaller reduction would probably be effected by attaching a hydrogen to an hydroxyl already linked to carbon, since the electrons are here more tightly bound, as evidenced by the lower refraction 3.23. Also, if the hydrogen were already attached to another oxygen, as pictured by Sidgwick for the alcohols, the forces which it exerted on the electrons of this oxygen would probably be weakened by its sharing with a second oxygen. This weakening would raise the refraction and thus tend to compensate for the reduction in the refraction of the other oxygen. An exact compensation, however, would be a very improbable coincidence. There is good reason then to believe that an association like that supposed by Sidgwick would bring about a reduction of 0.2 to 0.5 in the molar refraction of the alcohols. As the degree of association would be altered by mixing with another liquid and would vary with the concentration of the mixtures, the refraction of the alcohol should vary to an extent readily detectible in the results in Table II. The absence of such a variation provides evidence against the hypothesis of Sidgwick. If, however, the association is merely an orientation brought about by the powerful forces between the dipoles in the alcohol molecules, as discussed by two of the authors[4] in another connection, the forces of the electrons may not be sufficiently affected by change of concentration in the mixtures to alter the refraction by a detectible amount.

It has been found that the molar refraction of a pure substance in the vapor state at 100° is often from 1 to 3% higher than the refraction of the liquid at room temperature,[8] although for some liquids a decrease of about the same magnitude accompanies the rise in temperature and vaporization. The changes observed are of the same order of magnitude as the increases found by Falk to result from raising the temperature from 20 to 80°. Moreover, these changes are no greater for substances containing an hydroxyl group than for those supposed to be unassociated. For example, water vapor at 100° has a refraction 0.4 to 1.3% higher than the liquid at 10°, the values of different investigators varying; ethyl alcohol vapor at 100° is 0.7% higher than the liquid at 10°, the

---

[8] Lorenz, *Ann. Physik,* 11, 70 (1880); Prytz, *ibid.,* 11, 109 (1880); Brühl, *Z. physik. Chem*, **7**, 4 (1891).

supposedly unassociated ethyl ether is 1.4% higher in the vapor state at 100° and ethyl iodide is 0.9% higher, while methyl alcohol vapor at 100° is 0.3% lower than the liquid at 10°. The refraction of liquid n-heptyl alcohol increases 0.7% between 10 and 80" and that of the hydrocarbon, di-*iso*-amyl, increases by a similar amount. It is interesting to note that these increases are, in proportion to the temperature rise of 70°, of the same size as the increases, 1.6 to 1.9%, found by Smyth and Stoops[9] in the total polarizations of three isomers of heptane and an octane for a temperature increase of 180". As these substances have no electric moments, the total polarization is $P_E + P_A$ and P_A is found to have a value only about 3% of that of P_E for these isomers. It is evident that the alcohols fail to show a change of refraction greater than that shown by supposedly unassociated substances when not only the temperature but even the state is changed, although the association must decrease with rise of temperature and, for most of the substances, become negligible on vaporization. Just as the change in the degree of association almost certain to accompany change in the concentration of mixtures leaves the refraction unaffected within the limit of accuracy of the measurements, so the change produced by change of temperature has no distinguishable effect. Further evidence is thus brought to bear against the hypothesis of an actual sharing of electrons between molecules when association occurs in the alcohols and water.

Summary

The refractive indices for the sodium D line at 20° are measured for a large number of mixtures of fifteen different pairs of liquids.

The data are used to calculate the molar refractions of the liquids. It is found that the molar refractions of the components of the mixtures are independent of the concentration to within 0.07%. This proves that the contribution of induced electronic shifts to the polarization of a molecule of one of these substances is practically unaffected by the surrounding molecules.

The independence of composition shown by the molar refraction of the alcohols is used as evidence against the sharing of electrons between their molecules to bring about molecular association.

PRINCETON, NEW JERSEY

---

[9] Smyth and Stoops, THIS JOURNAL, 50, 1883 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

THE ATOMIC WEIGHT OF ANTIMONY FROM DIFFERENT SOURCES

BY R. K. MCALPINE

RECEIVED FEBRUARY 27, 1929 PUBLISHED JUNE 5, 1929

In 1923 Muzaffar[1] published a preliminary note under the above title in which he claimed that four samples of antimony, derived from rtibnites from Hungary, Borneo, Peru and Bolivia, gave by titration against potassium bromate atomic weights as follows: 121.14, 121.56, 121.72 and 122.37. In 1027 Krishnaswami[2] reported the results of comparisons of Kahlbaum's antimony with the metal obtained from four ores of Indian and Burmese origin. "A few trials were made of Muzaffar's method, but in spite of its apparent simplicity certain disadvantages became evident in practice and it was abandoned." Instead, the metal was converted to bromide and comparisons made of the bromide with silver and with silver bromide, copying the procedure that had been employed in this Laboratory.[3] A sentence from the conclusion tells the story: "The results are in good agreement with the best previous determinations; there is no indication that the variation is due to a change in atomic weight, and in any case such variation does not exceed 0.01 unit for the samples examined."

The present work was undertaken to review the work of Muzaffar using samples of antimony from the same sources and comparing them by density and by titration with potassium bromate. The materials used by Muzaffar had been exhausted, but through the kindness of Mr. C. T. Heycock under whose direction the work had been done it was possible to obtain some of the same ores from the supply house that had furnished the original materials. Since the extreme values were reported for the antimony obtained from Hungary and Bolivia, respectively, the ores from these countries were selected as sources of metal for detailed study.

Preparation of Materials

Antimony.—The metal was recovered by the same process that was used by the other workers. Following extraction with concentrated hydrochloric acid, the antimony was precipitated as oxychloride, dissolved in hydrochloric acid, oxidized with chlorine and several times recrystallized as metachloro-antimonic acid. This material was then hydrolyzed with water, the precipitate evaporated with nitric acid to remove chloride, ignited to oxide and reduced to metal by fusion with recrystallized potassium cyanide. The buttons thus obtained were cleaned mechanically and then alternately etched with nitric acid and fused in hydrogen until the latter process gave clear-surfaced globules which on solidifying formed crystalline masses with the highest luster on all surfaces.

---

[1] Muzaffar, THIS JOURNAL, **45, 2009 (1923).**

[2] Krishnaswami, **J.** *Chem. Soc.,* **2534 (1927).**

[3] Willard and McAlpine, THIS JOURNAL, **43,797 (1921).**

Throughout all these operations all reagents were specially purified and all utensils scrupulously cleaned, employing the technique used in the previous work in this Laboratory.[3]

Potassium Bromate.—Some of Kahlbaum's special reagent was recrystallized several times from redistilled water, using centrifugal drainage of the crystals and conducting the operations in quartz and platinum ware. The material thus obtained was dried in a desiccator over potassium hydroxide sticks. Qualitative tests for halide and chlorate were negative. A portion of this material was further dried by heating for three hours at 130° for use as a standard. A very small amount of water was still present, probably several hundredths of one per cent. A small portion of the stock has been reserved for a moisture determination which it is hoped to carry out before long.

Experimental

The experimental work may be divided into two parts: I, the determination of the density of antimony from different sources and II, the determination of the ratio of antimony to potassium bromate.

I. The Density of Antimony from Different Sources.—According to the theory of isotopic mixtures, if the atomic weight of an element varies with different specimens, the density of these specimens should also vary, and in direct proportion to the atomic weight. Since the values in question differ by slightly more than 1% in their extremes, a determination of the density should give an immediate check on variations of that magnitude.

Experimentally the method finally employed for this determination consisted in weighing the buttons of antimony in air and then in water and calculating their volumes from the differences in weights and the density of the water at the temperature used. A small platinum wire basket was constructed to hold the antimony. This was then suspended from the hook on the balance and weighed carefully. Then it was immersed in water to a fine knot on the suspension wire and weighed again. Next, after the basket had been carefully dried, an antimony button was placed in it and the system weighed as before, first in air, then in water. From these weights and the density of the water at the temperature of the experiment the density of the metal was then calculated.

Preliminary experiments showed that the ordinary round buttons of antimony gave erratic results. It appeared as if spaces were formed inside the buttons when they solidified, causing the apparent density to vary and to be lower than the true density. This difficulty was overcome in the following manner. A 20-centimeter hard glass tube was heated in an oxy-gas flame until the closed end was perceptibly cone-shaped for a length of three or four centimeters. The test-tube was then cleaned thoroughly. Next, the antimony was placed in the tube and a clean two-holed rubber stopper inserted bearing an inlet and an outlet tube for hydrogen. The antimony was then fused in hydrogen and after removing the flame the tube was rotated in such a way as to cause the metal to solidify as a shell in the cone-shaped part of the test-tube. With this manipulation it was found possible to get reasonably concordant results on repeated fusions followed by density determinations. The specimens of antimony were therefore prepared in this way and the densities determined, using redistilled water that was freshly boiled and cooled. In each case, after immersion in water, the surface of the shell was searched carefully for air bubbles. Only occasionally was one found. In such a case it was effectively removed by careful manipulation with a fine glass rod. Boiling to displace air was considered of doubtful value, because of *(a)* the chance for action of boiling water on the antimony and (b) the decrease in density noted by Cohen[4] when antimony was maintained for some time at 102–105°. Since the average value obtained here is slightly higher than that of Cohen[4] and still higher than that recommended by "International Critical Tables" (Vol. I, p. 104), the error due to trapped air must be very small. The results are given in Table I.

TABLE I

THE DENSITY OF ANTIMONY PROM DIFFERENT SOURCES

Source of antimony	Wt. of Sb in air, g.	Wt. of Sb in water. g.	Temp. of water, °C.	Density of Sb
Kahlbaum's	**15.3981**	**13.1024**	**22.3**	**6.694**
Hungarian stibnite	**14.9260**	**12.7342**	**22.3**	**6.703**
Bolivian stibnite (a)	**13.5033**	**11.4907**	**22.3**	**6.696**
(b)	**12.9599**	**11.0275**	**22.3**	**6.695**

The inherent limitation of this method lies in the sluggish action of the balance when weighing in water. It was found possible, however, to determine the resting point of the balance to within one milligram; therefore the error in weighing, with two weighings in water involved, should not exceed two milligrams at the maximum. Since the weight of displaced water is approximately two grams, the density values should check within 0.1%.

The figures in Table I give no evidence of variation in the density of antimony from different sources. The variations from the average, +0.006 and −0.003, are within the limits of the method used. Even if the attempt were made to attach significance to these variations it would be noted that their indications are at variance with the work of Muzaffar, not only as regards magnitude, but also in direction. He reported 121.14 for the atomic weight of antimony from Hungary and 122.37 for that from Bolivia. On that basis the density of the antimony from Bolivia should be highest, Kahlbaum's antimony intermediate, corresponding to the atomic weight 121.77, and that from Hungary lowest.

II. The Ratio of Antimony to Potassium Bromate.—In analytical work the bromate method for antimony is recognized as one capable of distinct accuracy, but the size of the sample is commonly limited to two or three-tenths of a gram of metallic antimony. Since it was desirable to

---

[4] Cohen and van den Bosch, *Z. physik. Chem.*, 89, 757 (1915).

use larger samples to increase the accuracy of the determination, some preliminary experimentation was necessary to work out a satisfactory procedure. In these studies it was found that a sample as large as three grams could be converted to sulfate readily by digesting at near the boiling point with fifty milliliters of concentrated sulfuric acid. On cooling a considerable amount of antimony sulfate crystallized out, but this dissolved readily in dilute hydrochloric acid. The usual procedure recommends that the final solution contain approximately 20% by volume of concentrated hydrochloric acid, and be titrated with methyl orange as indicator at not less than 60°. With the large amount of sulfuric acid already present it was found that a lower concentration of hydrochloric acid gave better results, both in sharpness of end-point and in completeness of oxidation of the antimony by the bromate. It was also found that the reaction proceeds readily at room temperature, making it possible to add the bromate in solid form, swirl to dissolve the bromate, then heat to the proper temperature to obtain a sharp end-point and complete the titration. To avoid error in the transfer of the bromate it was found convenient to weigh the salt into a small shell vial, ten by thirty centimeters in size, and then drop vial and all into the solution, taking care to avoid spattering. This operation was carried out in a flask that could be stoppered until all of the bromine fumes were absorbed by the solution, thus avoiding error from loss of bromine. In the final determinations the following method was used.

A sample of 2 to 3 g. of antimony was weighed out, transferred to a half-liter glass-stoppered Erlenmeyer flask and treated with 50 ml. of concentrated sulfuric acid; the flask was covered with a watch glass and heat applied with a small flame until the metal was dissolved. This required one-half to three-quarters of an hour. As soon as the reaction was complete the flame was removed and when cool enough to permit it the flask was placed in running water for a few minutes. Then there was added 350 ml. of dilute hydrochloric acid containing 10% by volume of the concentrated acid, the cover glass and walls of the flask being rinsed with acid of the same strength. The solution was boiled for several minutes to remove sulfur dioxide, using a current of carbon dioxide to prevent access of oxygen from the air and continuing the process for two or three minutes after the odor had disappeared. The solution was then cooled in running water, with the atmosphere of carbon dioxide maintained, and when cold the glass stopper was inserted. Meanwhile an amount of potassium bromate was weighed out 3 to 5 mg. less than sufficient to oxidize the antimony. The stopper was then removed and the vial containing the bromate dropped in, the stopper reinserted and the solution swirled until the salt was completely dissolved and the solution again colorless. This required only two or three minutes. The cold solution was allowed to stand for about five minutes longer for complete absorption of any bromine fumes, then the stopper was removed, the solution heated to 60–70° under an atmosphere of carbon dioxide, three drops of methyl orange solution added and the titration completed with a standard solution of potassium bromate containing one milligram of the salt per milliliter. In some cases duplicate titrations were carried out by reducing with sulfur dioxide and repeating the above operations, starting with the removal of excess sulfur dioxide by boiling in a current of carbon dioxide. The blank to determine the correction to be applied for the end-point showed that one-tenth of a milligram of potassium bromate was sufficient to destroy the color of the indicator under the conditions used.

Table II gives the results of comparison of the different specimens of antimony with each other by titration with potassium bromate.

TABLE II

THE RATIO OF POTASSIUM BROMATE TO ANTIMONY FROM DIFFERENT SOURCES

			$KBrO_3$ added			Ratio	
Source	Sample, g.	Titrn.	solid g.	soln. ml.	total g.	$\frac{KBrO_3}{Sb}$	Ratio calcd.
Kahlbaum	2.3965	1st	1.0915	6 1	1 C976	0.4580	0 4571
(preliminary)		2nd	1 0928	3 4	1 0962	4574	4571
		3rd	1 0928	2 4	1 (9.52	4570	.4571
Kahlbaum[a]	2.1560	1st	0 9829	4 5	0 9874	.4580	.4571
Hungary[a]	2 1234	1st	0 9679	5 1	0 9730	4582	4571
		2nd	0 9661	6 5	0 9726	.4580	4571
	2 8452	lst[b]					
		2nd	1 2958	6 0	1 3018	4575	4571
Bolivia[a]	2 0906	1st	0 9526	4 3	0 9569	4577	.4571
		2nd	0 9512	5 6	0 9568	4577	.4571
	2 0695	1st	0 9434	4 4	0 9478	4580	.4571

[a] Pieces of shell from density determination.

[b] In this determination, through error in calculation, an excess of potassium bromate was added as solid so the first titration was lost.

In examining the data in Table II two points are to be noted: first, that with repeated titrations the ratio of potassium bromate to antimony falls off slightly; second, that comparisons of the ratios for first titrations show a concordance indicating the essential identity of the different specimens of antimony. The average ratio for first titrations is 0.4580 and the maximum variation from this—0.0003—is shown between the two samples of antimony from Bolivia. This shows that the atomic weights of the different specimens of antimony studied are identical within 0.05 unit of each other in contrast to a difference of 1.23 reported.

Concerning the true ratio of potassium bromate to antimony, the value calculated from the accepted atomic weights is 0.4571. The average ratio for first titrations, 0.4580, is obviously too high because of the presence of a slight amount of moisture in the potassium bromate. It is doubtful, however, if the moisture alone would be sufficient to account for this difference. Further, the decrease in ratio with successive titrations suggests the possibility that the reaction of antimonous chloride with potassium bromate is not quite so simple as represented by the ordinary equation. This reaction is capable of experimental investigation, but since it does not affect materially the question of the atomic weights of antimony from different sources it has been set aside for the moment.

It is hardly worth while to speculate on the errors of Muzaffar's work. The paper as originally presented for publication contained density determinations indicating variations corresponding to the atomic weights reported. These were omitted in the published article, as well as several of the crudities noted in other parts of the work. In the paper as published the experimental details are lacking that should be considered if critical comment were to be made. The most charitable view, however, would be that he attempted the application of procedures to unknown material before he had tested them sufficiently to understand their behavior on known material, a not uncommon mistake in analytical work.

Summary

1. Muzaffar reported atomic weights of **121.14** and 122.37, respectively, for specimens of antimony derived from stibnites from Hungary and from Bolivia.
2. Specimens of metallic antimony have been prepared from stibnites from Hungary and Bolivia, the ores being obtained from the supply house that furnished the material for Muzaffar.
3. These specimens have been compared with each other and with Kahlbaum's antimony by density determinations and by titration with potassium bromate.
4. The densities of the three specimens lie within one-tenth of one per cent. of one another.
5. The ratios of potassium bromate to antimony lie within five-hundredths of one per cent. of each other.
6. There is no evidence of variation in the atomic weight of antimony from different sources.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE CHEMICAL LABORATORY OF THE UNITED GAS IMPROVEMENT COMPANY]

THE SHIFT IN THE 1.14μ ABSORPTION BAND OF SOME BENZENE DERIVATIVES

BY JAMES BARNES AND W. H. FULWEILER

RECEIVED FEBRUARY 28, 1929 PUBLISHED JUNE 5, 1323

In an earlier paper[1] by the authors it was shown that the frequencies of the absorption bands (at approximately 0.87μ) of benzene and some of its derivatives are shifted progressively toward lower values as methyl and ethyl groups are added to the benzene ring. This note is to report that a similar effect has been observed in benzene, toluene, p-xylene and mesitylene in their next outstanding absorption band toward the infra-red, which has a wave length of approximately 1.14μ. The amount of the shift is the same within the limit of error as that observed in the 0.87μ band.

The apparatus used, namely, source of continuous radiation, six-foot

---

[1] **Barnes** and **Fulweiler,** THIS JOURNAL, **49,2034 (1927).**

Rowland concave grating and thalofide cell, as well as the method of measurement, were the same as those described in the *Physical* **Review,** 32, 618 (1928). In addition, **a** No. 87 Wratten filter was placed in front of the slit of the grating spectrometer.

The results obtained with an absorption cell **30** mm. in length are recorded by small circles on the curves of Fig. 1. These curves show the variation in the transmission ratio with wave length for the hydrocarbons used. In order clearly to separate the curves the zeros of the transmission ratio for the different liquids are uniformly raised along the ordinate axis. The wave-length scale is, however, in the same position for each liquid.

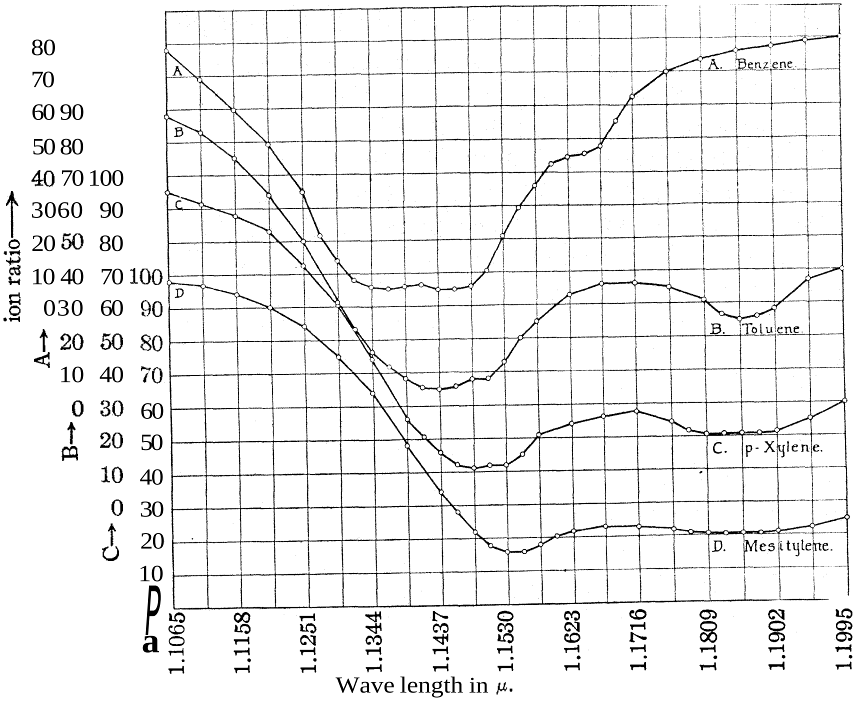


Fig. 1.—Variation of transmission ratio with wave length for benzene derivatives.

Inspection of these curves shows that the wave length of the center of the outstanding absorption band is shifted toward the region of longer wave length and hence the frequency of the oscillator is decreased as methyl groups are added to the benzene ring. They also show that the addition of this group appreciably lowers the transmission in the region from 1.16μ to 1.20μ, with a broad and weak absorption band at approximately 1.185,~.

The following table gives the wave length, λ(μ), of the center of this outstanding absorption band for each of the liquids investigated. The values are believed to be accurate within ±0.001μ.

TABLE I

WAVE LENGTHS OF ABSORPTION BANDS OF BENZENE DERIVATIVES

Derivative	Benzene	Toluene	p-Xylene	Mesitylene
$\lambda(\mu)$	1.1409	1.1442	1.1498	1.1539

BRYN MAWR, PENNSYLVANIA

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

THE EFFECT OF AIR ON THE POTENTIAL OF THE MERCURY–MERCUROUS SULFATE ELECTRODE

BY MERLE RANDALL AND HENRY A. STONE

RECEIVED MARCH 13, 1929 PUBLISHED JUNE 5, 1929

Vosburgh[1] has shown that the potential of Weston standard cells with slight additions of basic mercuric sulfate to the mercury–mercurous sulfate electrode in neutral or slightly acid saturated cadmium sulfate solutions or prepared with the materials in contact with air is about 0.03 mv. higher than that of cells prepared out of contact with the air. Randall and Young[2] found relatively large errors of the order of 1.5 mv. in acid calomel electrodes prepared in the presence of air. We shall here study the effect of air on the hydrogen–mercurous sulfate–mercury cell.

The Reaction between Dilute Sulfuric Acid and Mercury.—Redistilled mercury and 0.1 *M* sulfuric acid were sealed in pyrex flasks[2] and rotated for twenty-four hours in a thermostat at 25°. In some of the flasks the air was displaced with a current of pure nitrogen and acid which had been freed from air by boiling in a current of pure nitrogen was used. There was no evidence of the formation of a precipitate but upon the addition of air-free dilute hydrochloric acid a precipitate of mercurous chloride appeared in the acid from the flasks in which no precautions had been taken to exclude air.

Materials.—The sulfuric acid was prepared and analyzed as described by Randall and Scott.[3] Nitrogen was prepared by passing commercial nitrogen over three feet of reduced copper turnings at a bright red heat, or by adding a small amount of hydrogen and passing the mixed gas over white-hot platinum wire. The dilute acids were prepared from the stock acid by dilution with conductivity water (weight burets, concentration in moles per 1000 g. of water in vacuum) and traces of air were removed by bubbling through pure nitrogen for eight hours. The acids were stored in quartz flasks.

Mercurous sulfate was prepared by precipitation in the dark from mercurous nitrate.[4] It was washed six to eight times with air-free acid in an atmosphere of nitrogen in the pipet (Fig. 1) and introduced into the cell by a slight adaptation of the method of Vosburgh.[1] Considerable care was taken to shield the mercurous sulfate from the light. We found that mercurous sulfate in contact with 0.1 M sulfuric acid

---

[1] Vosburgh, THIS JOURNAL, 47, 1255 (1925).

[2] Randall and Young, *ibid.*, 50, 989 (1928).

[3] Randall and Scott, *ibid.*, 49, 636 (1927).

[4] Prepared by the method of Randall and Frandsen (unpublished); see ref. 2.

had turned yellowish-brown after two months' contact with mercury in the half-cells which had been submerged in the oil thermostat at 25° in a moderately lighted room.[5] In the experiment quoted here the outside of the half-cells was coated with black "Duco" lacquer.

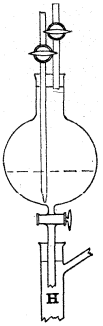


Fig. 1.—Pipet.

Cells.—The hydrogen electrode was the usual type.[2] The essential parts of the mercury–mercurous sulfate half-cell are shown in Pig. 2. To insure the absence of air a current of pure nitrogen was used to displace the sir in the apparatus assembled as shown, with stopcocks A, B and C open and D and E closed. The stopper F of the half-cell H was then quickly withdrawn (with an increased current of nitrogen), the mercury introduced and then the pipet (Fig. 1) containing the air-free suspension of mercurous sulfate in the sulfuric acid replaced the stopper. The mixture of paste and acid then filled the cell to the level of the side arm, and while the current of nitrogen was continued the pipet was withdrawn and the cell again quickly sealed by the stopper F. (The pipet could have been left in the cell.) The stopcock A was now closed and acid introduced into the reservoir I and bubbled with pure nitrogen, the cell painted with black "Duco" and then transferred to the thermostat with the oil level as indicated by the dotted line. The current of nitrogen was replaced by a current of electrolytic hydrogen which had passed over a white-hot filament to remove traces of oxygen. After three days the sulfuric acid in the cell was replaced by flushing the cell by opening stopcock A. The intermediate vessel J was filled, stopcock C closed, the tube leading to D filled and this stopcock closed. The acid was then removed through C until flushing was complete. Contact with the hydrogen electrode was made through the greaseless stopcock E, the tube leading to J being filled with acid brought from the hydrogen electrode vessel. The stopcock B also connected to a second mercury–mercurous sulfate half-cell. The flushing was usually done in the evening and reading commenced on the following morning. The cells came to equilibrium in from twenty-four to forty-eight hours and were constant to less than a maximum difference of 0.03 mv.

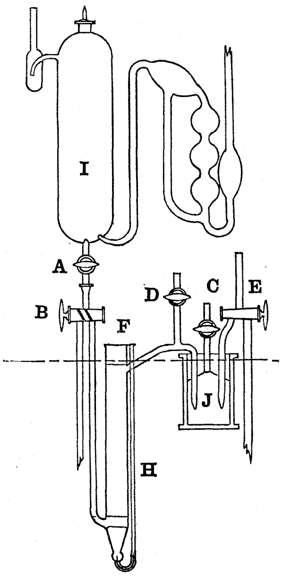


Fig. 2.—Half-cell.

---

[5] Similar discolorations have been noted by (a) Hulett, *Phys. Rev.*, 32, *262* (1911); (b) Obata, *Proc. Phys. Math. Soc., Japan,* **(3)** *2*, 79, 223 (1920) and (c) Horsch, THIS JOURNAL, 41, 1787 (1919), who stated that the discoloration (in the presence of zinc sulfate) would not take place if a small concentration of hydrogen ion was present.

Potential Measurements.—After three days moist air was introduced at the surface of the mercury, at first only a few bubbles and later as much as a liter. Initial values from 0.2 mv. to 0.4 mv. lower were obtained but in fifteen minutes the cells would be back to their normal voltage and remained constant as before for thirty days. Replacing the electrolyte produced no change in the potential.

The following values of the hydrogen–mercury–mercuroussulfate cell are shown in Table I.

TABLE I

VALUES OF THE HYDROGEN–MERCURY–MERCUROUS SULFATE CELL

Molality of sulfuric acid	0.1000	0.2101
Exptl. e.m f., volts	0.73694	0.71858
Interp. e.m f. (R. and C.)[6]	0.73697	0.71852

Summary

Mercury is dissolved by dilute sulfuric acid containing air.

The effect of air upon the potential of the mercury–mercurous sulfate electrode in moderately concentrated acid solution is negligible when the electrodes are prepared in the usual manner.

BERKELEY, CALIFORNIA

NOTE

Sodium Maleate—A Buffer for the PH Region of 5.2 to 6.8.—In the course of a research on autoxidation the author has found that the buffering range of sodium hydrogen maleatesodium hydroxide mixtures extends from a PH of 5.2 to 6.8, giving maximum buffering power in the region where phthalate and phosphate buffers have the least. The lower valence of the ions results in a smaller salt effect than is the case with citrate buffers.

Sodium hydrogen maleate is easily prepared in pure form as $NaHC_4H_2O_4 \cdot 3H_2O$.[1] The following method was found convenient. A liter of aqueous solution containing 250 g. of maleic acid was exactly halved. To the first half was added 6 N sodium hydroxide until the precipitate first formed had redissolved, then normal sodium hydroxide to the neutral point. The two halves were mixed, cooled in an ice-bath and the crystallized salt was filtered off. Recrystallization is very easy. One recrystallization was found sufficient for a product made from Kahlbaum acid. When dried in a warm place in the open room, the salt conforms exactly to the trihydrate formula and may be weighed as such. Preliminary tests indicated that it might even be used as a primary standard in acidimetry.

[6] Randall and Cushman, THIS JOURNAL, 40, 393 (1918).

[1] Biichner, *Ann.*, 49, 64 (1844); Weiss and Downs, THIS JOURNAL, 45, 2342 (1923).

The following table gives the composition of mixtures for P_H values from 5.2 to 6.8, as taken from a curve constructed from several titrations with a quinhydrone electrode against a saturated calomel cell at 25°.

TABLE I

COMPOSITIONS OF MIXTURES (TAKEN FROM CURVE)

Fifty cc. of $N/5$ sodium hydrogen maleate in each case; diluted to 200 cc.

P_H	5.2	5.4	5.6	5.8	6.0	6.2	6.4	6.6	6.8
$N/5$ NaOH, cc.	7.2	10.5	15.3	20.8	26.9	33.0	38.0	41.6	44.4

The base was added from a buret to a maleate solution containing 0.109 g. of quinhydrone. The region of each titration was small, so that the total volume could be kept within limits of 100 ± 3 cc. Potentiometric measurements of the cell

Au | buffer–quinhydrone | sat. KCl | sat. calomel cell

were used for calculation of P_H according to the usual method,[2] ignoring salt effect and contact potentials. Results from several titrations over different regions, comprising twenty-five measurements, were united into a single curve, from which the above figures were interpolated.

CONTRIBUTION NO. 570 FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

J. W. TEMPLE

RECEIVED FEBRUARY 26, 1929
PUBLISHED JUNE 5, 1929

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SOME PHTHALEINS OF THE TRIHYDROXYPHENOLS[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

RECEIVED AUGUST 27, 1928 PUBLISHED JUNE 5, 1929

In several previous papers data have been presented on the absorption spectra of the benzeins and phthaleins derived from some of the mono- and dihydroxybenzenes, for example, phenol,[3] *o*-cresol,[3] resorcinol[4] and hydroquinol.[5] The present study of the trihydroxy derivatives includes

[2] Biilmann and Lund, *Ann. chim*, 16,321 (1921).

[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

[3] Orndorff, Gibbs and co-workers, THIS JOURNAL, (a) 47, 2767 (1925); (b) 48, 1994 (1926); (c) 49, 1545 (1927); (d) 49, 1588 (1927); (e) 50,2798 (1928).

[4] Orndorff, Gibbs and Shapiro, *ibid.*, (a) 48, 1327 (1926); (b) 50, 819 (1928); (c) 50, 1755 (1928).

[5] Shapiro, *ibid.*, 50, 1772 (1928).

the benzein,[6] phthalein and sulfonephthalein[7] of pyrogallol, the phthalein and sulfonephthalein[8] of hydroxyhydroquinol and the sulfonephthalein of phloroglucinol.[9]

With the extensive data now available a number of significant generalizations have become evident, which clearly indicate that definite conclusions may be drawn from absorption spectra both regarding the structure of these triphenylmethane compounds and their chemical properties, but these will be elaborated in greater detail in a later paper. The effect produced on the chemical properties and on the nature of the absorption by the introduction of hydroxyl groups in the phthaleins is a function both of their number and position. Thus the acidic properties of the sulfonic acid radical in the sulfonephthaleins are greatly influenced by the nature of the substitution in the two phenolic residues. The tendency to form an inner salt may be taken as a qualitative measure of the dissociation constant of the acid group, and a reliable indication of the existence and stability of such a salt is furnished by the similarity of the absorption spectra of the neutral and acid solutions. Thus hydroquinolsulfonephthalein appears as a stronger acid than either phenol- or o-cresolsulfonephthalein, for it shows the same type of absorption in aqueous, alcoholic and sulfuric acid solutions,[5] while the two latter compounds exhibit the inner salt structure in alcoholic solution but the quinoid hydrate configuration in aqueous solution.[3e] The addition of a molecule of water to form the hydrate necessitates the rupture of the inner salt bond and hence points to a lesser stability of the latter structure in the phenol and o-cresol compounds than in the hydroquinol derivative. By an independent method, B. Cohen[10] has demonstrated the weakening of the acidic properties of the sulfonephthaleins due to alkyl substitution in the meta position to the phenolic hydroxyl and it is hoped to check these conclusions by the spectroscopic method outlined above. If it is granted that the introduction of hydroxyl groups serves to enhance the acid properties, it is to be anticipated that the carboxyl radical, ordinarily a very weakly dissociable acid group, will have its dissociation constant so increased in a sufficiently hydroxylated phthalein as to render the formation of an inner salt possible. This has now been realized with hydroxyhydroquinolphthalein, whose solutions in absolute alcohol and in concd. sulfuric acid exhibit closely analogous absorption spectra, which in turn closely resemble those obtained for the corresponding solution of hydroxyhydroquinol*sulfone*phthalein, as pointed out below. The effect of the position of the hydroxyl groups on these

---

[6] Orndorff and Wang, THIS JOURNAL, 47, 290 (1925); 49, 1284 (1927).

[7] Orndorff and Fuchs, *ibid.*, 48, 1939 (1926).

[8] M. L. Willard, "Dissertation," Cornell University, 1927.

[9] We are indebted to Dr. Barnett Cohen of the Public Health Laboratory, Washington, D. C., for the pure sample of this compound.

[10] B. Cohen, *Public Health* Reports, 41, 3051 (1926).

properties is clearly demonstrated by pyrogallolphthalein, or gallein, which is isomeric with hydroxyhydroquinolphthalein but whose absorption spectrum in absolute ethanol is typical of the lactone structure, indicating that its carboxyl radical has the usual weakly acid function that occurs in the other lactoid phthaleins.

Discussion of the Absorption Spectra

The curves for the absorption spectra of the pyrogallol derivatives in absolute ethanol solution are shown in Fig. 1. Curve A for pyrogallolbenzein, Curve B for pyrogallolphthalein (gallein) and Curve C for pyrogallolsulfonephthalein (sulfonegallein) represent three distinct types of absorption and hence indicate that each of these related compounds possesses a different internal structure. The absorption curve of pyrogallolbenzein bears a general resemblance to the curve obtained for resorcinolbenzein[4a] and is regarded as evidence for the existence of these compounds in the quinoid state and not as quinoid hydrates. In such cases where hydrate formation is definitely known to take place, as previously observed with benzaurin[3c] (phenolbenzein) and *o*-cresolbenzein,[3d] fading of the solution occurs due to the setting up of an equilibrium between the colored hydrate and the colorless carbinol, and the absorption in the ultraviolet region is characterized by the presence of several weak bands, of which two have been found to be typical of the benzenoid state in triphenylmethane derivatives.[11] Neither fading nor the development of the above typical bands has been observed with pyrogallol- or resorcinolbenzein.

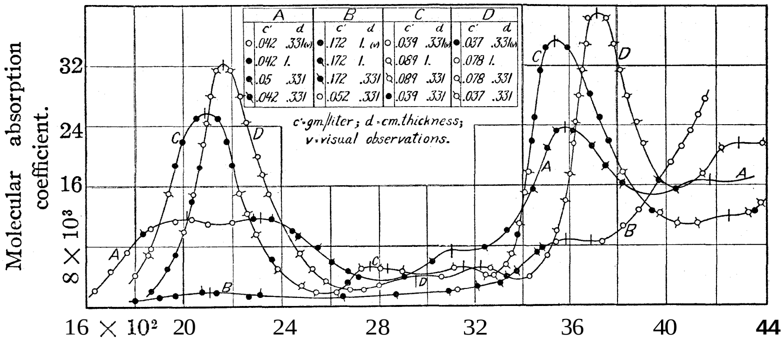


Fig. 1.—Neutral absolute ethanol solutions: A, pyrogallolbenzein; B, gallein; C, sulfonegallein; D, dimethyl ether of sulfonegallein.

The absorption spectrum of gallein in absolute ethanol, Curve B, is marked by a weak band in the visual region and by two weak bands of nearly equal intensity in the ultraviolet at frequency numbers 3583 and 3693, having a separation of 110 mm.$^{-1}$. In position, separation and in-

[11] Gibbs and Shapiro, Proc. *Nat.* Acad. *Sci.*, 14, 251 (1928).

tensity these two bands correspond closely with the characteristic pair of bands found for numerous other lactoid phthalein derivatives.[11] It therefore appears certain that gallein, despite its color in the solid state and in neutral solution, is present primarily as the lactone. The band at 2107 responsible for the color of the solution may be related to the near ultraviolet band found in the colorless neutral solutions of hydroquinolphthalein[5] and of phenol- and *o*-cresoltetrachlorophthaleins,[3e] but shifted into the visual region because of the addition of hydroxyl groups or, what is more likely, it may be due to the presence of a small amount of the quinoid form, in equilibrium with the lactone. The closely related tetrachlorogallein is an almost colorless compound and has been considered by Orndorff and Delbridge[12] as being primarily lactoid, but containing a small percentage of the quinoid modification.

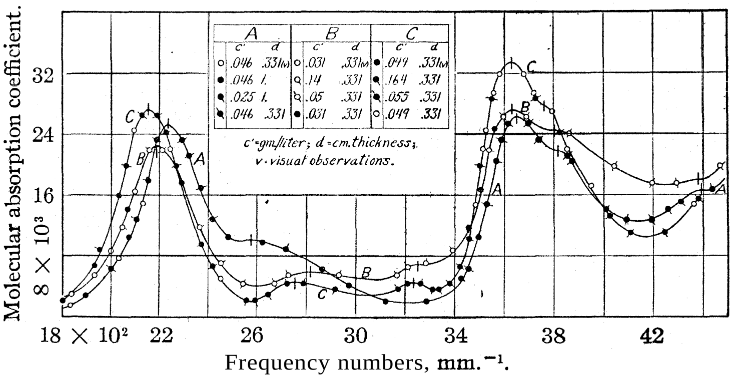


Fig. 2.—Concd. sulfuric acid solutions: A, pyrogallolbenzein; B, gallein; C, sulfonegallein.

Sulfonegallein exhibits absorption, Curve C, which is very similar to that of its sulfuric acid solution, Fig. 2, Curve C. Since in the latter solvent salt formation occurs on the basic, quinoid oxygen atom, this type of absorption is evidently characteristic of a salt structure and hence is the basis for assigning the inner salt configuration to sulfonegallein in neutral ethanol solution. Orndorff and Fuchs[13] arrived at the same conclusion from the fact that sulfonegallein does not react with hydrogen chloride gas, which indicates that the basic properties have already been neutralized. Sulfonegallein takes on a molecule of water at the oxygen atom of the pyrone ring, giving rise to pyrogallolsulfonephthalein, but the latter compound shows exactly the same absorption as the former in all solvents. The existence of the pyrone ring thus plays no part in determining the optical properties of the compound, a conclusion which was reached previously on comparison

---

[12] Orndorff and Delbridge, *Am. Chem. J.*, **42**, 183 (1909).

[13] Ref. 7, p. 1943.

of phenolphthalein and fluoran.[4b] Curve D of Fig. 1 shows the absorption of the dimethyl ether of sulfonegallein in absolute ethanol and is of the same type as Curve C for sulfonegallein but is shifted bodily toward the ultraviolet. As this evidence indicates that the dimethyl ether must likewise be considered as an inner salt, it follows that methylation of two of the hydroxyl groups has no radical effect on the nature of the molecule.

Figure 2 presents the absorption spectra of the sulfuric acid solutions of the pyrogallol derivatives. The general similarity of the curves is striking and affords sufficient basis for postulating identical quinoid salt structures for the three compounds in this solvent. Attention is called to the characteristic double band, in the region of frequency numbers 3600–3800, which has been found for the sulfuric acid solutions of nearly all phthaleins containing the pyrone ring, such as fluorescein,[4b] sulfonefluorescein[4c] and the hydroxyhydroquinol derivatives described below. The hydroquinol and phloroglucinol compounds have proved exceptional in this respect.

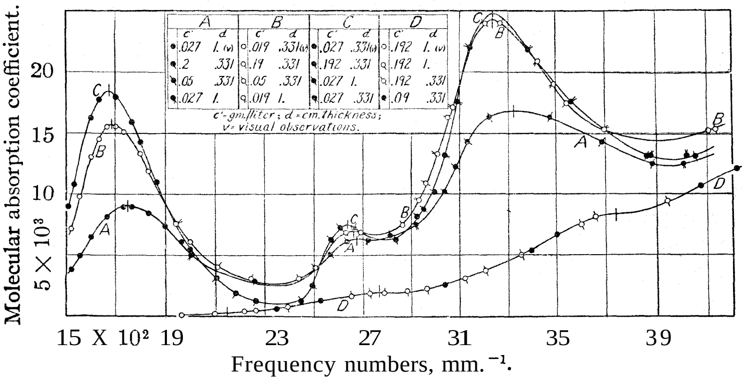


Fig. 3.—Aqueous alkaline solutions. A, pyrogallolbenzein in 5% KOH; B, gallein in 33% KOH; C, sulfonegallein in 33% KOH; D, sulfonegallein—faded.

The freshly prepared aqueous alkaline solutions, pyrogallolbenzein in 5% potassium hydroxide and gallein and sulfonegallein in 33%, also exhibit closely related absorption spectra, as shown in Fig. 3. It is noted in passing that pyrogallolbenzein, like resorcinolbenzein,[4a] is not soluble in solutions of potassium hydroxide greater than 5%. Unlike resorcinolbenzein and in common with the other pyrogallol compounds, its alkaline solution is not fluorescent and rapidly fades to a very pale yellow in the course of a few days. It is probable that the lesser intensity of the absorption of its freshly prepared solution, Curve A, as compared with Curves B and C for gallein and sulfonegallein, respectively, is due to a somewhat greater incipient fading. However, the similarity in form and position of the bands indicates the existence of basic salts of identical structure in alkaline solution, even though pyrogallolbenzein, lacking an acidic radical, forms only a *tri*basic salt, while the others are converted into tetrabasic salts. The fading of these solutions, which was complete in three to four days, is due to the formation of salts of the colorless, benzenoid carbinol, in a manner entirely analogous to the behavior of phenolphthalein in strongly alkaline solution. The absorption spectra of the faded solutions are fairly similar and are characterized by the presence of three shallow bands superimposed on a background of weak general absorption, as illustrated by Curve D for the solution of sulfonegallein measured five days after its preparation. Owing to the difficulty of accurately locating shallow bands of this type, their positions are given only approximately in round numbers. Table I summarizes the locations of all the bands for the above pyrogallol compounds in the various solvents employed.

TABLE I

FREQUENCY NUMBERS OF BANDS IN SOLUTIONS OF PYROGALLOL COMPOUNDS

		Pyrogallolbenzein					
Absolute ethanol		2015	2315	3100	3582	4175	
Concd. sulfuric acid		2236	2577	3651	3816	4395	
5% potassium hydroxide	Fresh	1750	2673	3322			
	Faded	2120	3005	3995			
		Gallein					
Absolute ethanol		2107	3583	3693			
Concd. sulfuric acid		2188	2817	3249	3631	3804	4383
33% potassium hydroxide	Fresh	1685	2660	3234			
	Faded	2150	2845	3700			
		Sulfonegallein					
Absolute ethanol		2089	2761	2833	3151	3539	4250
Concd. sulfuric acid		2156	2755		3232	3630	3763
33% potassium hydroxide	Fresh	1675	2635	3235			
	Faded	2150	2765	3740			
		Dimethyl Ether of Sulfonegallein					
Absolute ethanol		2166	2952	3223	3722	4290	

Figure 4 presents the absorption spectra of absolute ethanol solutions of hydroxyhydroquinolphthalein, Curve A, hydroxyhydroquinolsulfonephthalein, Curve B, and phloroglucinolsulfonephthalein, Curve C. The two hydroxyhydroquinol derivatives have almost identical absorption, the phthalein showing slightly greater intensity and having its bands shifted slightly toward the ultraviolet with the exception of the one at 3055, which is to the red side of the corresponding band for the sulfonephthalein. This is the first instance in the course of our study of the phthaleins, where a phthalein and sulfonephthalein of a given phenol have shown the same type of absorption in ethanol solution. Taking into account the fact that their sulfuric acid solutions, Fig. 5, Curves A and B, also have absorption of this type, it is evident on the basis of the criterion already established and verified, that hydroxyhydroquinolphthalein must possess the structure of an inner salt and hence that its carboxyl group has acidic properties equivalent to those of the sulfonic acid radical. Such a marked increase in the dissociation constant of the carboxyl group as the result of substitution in the molecule is, of course, not without precedent, as note, for example, acetic and trichloro-acetic acids. The objection that the active substituents are far removed from the affected carboxyl group, since they are located in different phenyl nuclei, is met by

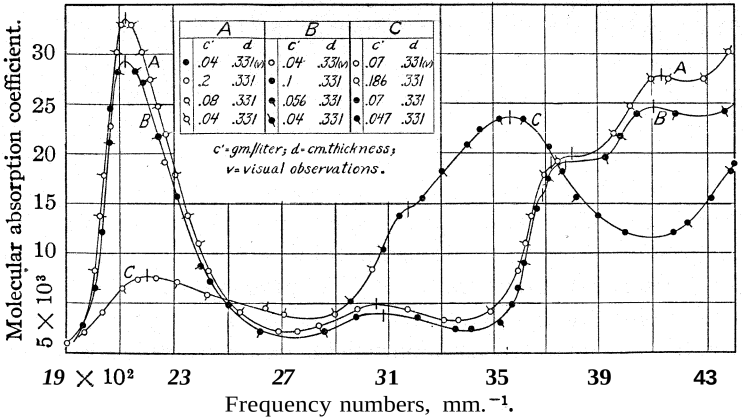


Fig. 4.—Neutral absolute ethanol solutions: A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonephthalein; C, phloroglucinolsulfonephthalein.

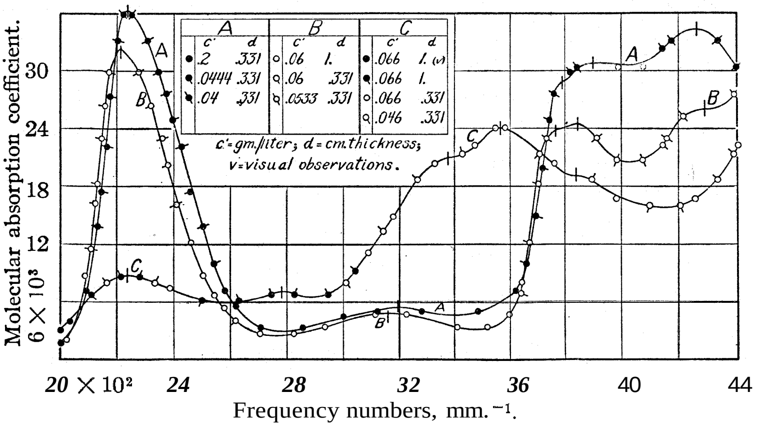
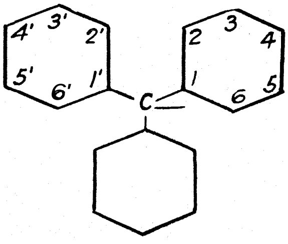


Fig. 5.—Concd. sulfuric acid solutions: A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonephthalein; C, phloroglucinolsulfonephthalein.

considering that any change in the distribution of chemical forces in a given benzene ring is transmitted to the rest of the molecule through its point of linkage, which in this case is the methane carbon atom and this in turn is in the ortho position to the acid radical.

The absorption spectra of phloroglucinol in absolute ethanol, Curve C, Fig. 4, and in concd. sulfuric acid, Curve C, Fig. 5, while alike in type, are entirely different in character from those of the hydroxyhydroquinol derivatives. In general it has been noted that those quinoid phthaleins which have a different number or arrangement of phenolic hydroxyls, have quite different absorption spectra. Thus each of the sulfonephthaleins derived from the following phenols has its own peculiar absorption: phenol (or 4,4′-dihydroxydiphenylsulfonephthalide), hydroquinol (anyhydro-2,2′,5,5′-), resorcinol (anhydro-2,2′,4,4′-), pyrogallol (2,2′,3,3′,4,4′), hydroxyhydroquinol (anhydro-2,2′,4,4′,5,5′-), and phloroglucinol (anhydro-2,2′,4,4′,6,6′-).[14] *o*-Cresolsulfonephthalein, however, which is a dimethyl derivative of phenolsulfonephthalein and which has its phenolic hydroxyls in the same relative position, 4,4′-, as phenolsulfonephthaiein, shows the same type of absorption spectrum as that compound.[3e] Similarly the dimethyl ether of sulfonegallein, in which two of the phenolic hydrogen atoms are replaced by methyl groups, absorbs in the same manner as its parent substance (see above). On the other hand, all the lactoid phthaleins, as well as lactoid derivatives of the quinoid phthaleins, have been shown to possess related absorption spectral[1] regardless of the number and position of the hydroxyl groups. A possible explanation of this difference in optical behavior on the part of the quinoid and lactoid phthaleins may be that with the former the molecule is in a much less stable condition, as indicated by the generally greater reactivity of such compounds, and that the introduction of active groups, such as hydroxyl, can therefore produce a marked effect on the distribution of interatomic forces with a corresponding effect on the absorption spectrum.

Figure 6 exhibits the absorption spectra of freshly prepared solutions of hydroxyhydroquinolphthalein and -sulfonephthalein and of phloroglucinolsulfonephthalein in 33% aqueous potassium hydroxide. Curves A and B for the two hydroxyhydroquinol derivatives, respectively, are fairly parallel and are characterized by a relatively complex set of six bands. Both



---

[14] The numbering of the positions of the hydroxyl groups is based on the schematic structure indicated. Where hydroxyl groups are present in the 2,2′-positions and water is split off to form the pyrone ring, the word anhydro- is prefixed.

solutions fade in a few days to a very pale yellow and their absorption spectra, represented here by that of hydroxyhydroquinolphthalein, Curve C, are found to have practically the same bands, except for the disappearance of the one in the visual region, as curves for the fresh solutions. Owing to the general flattening out of the absorption curve it is much more difficult to locate these bands precisely, This type of behavior is, however, different from that of the other phthaleins on which measurements have been obtainable before fading occurred, since in these cases the absorption spectrum was different for the fresh and faded solutions. Phloroglucinolsulfonephthalein in strong alkali yields a solution of an orange-yellow color, quite unlike the well-known red or bluish-red of alkaline solutions of the other phthaleins, and is also exceptional in that no fading was observed over a period of several months. Its absorption, Curve D, is marked by three broad bands.

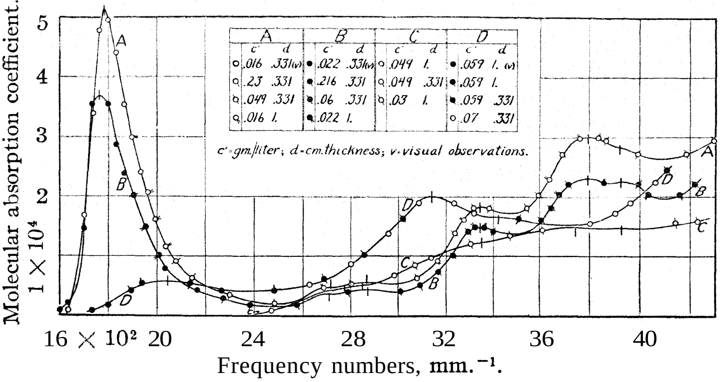


Fig. 6.—33% aqueous potassium hydroxide solutions. A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonephthalein; C, hydroxyhydroquinolphthalein—faded; D, phloroglucinolsulfonephthalein.

The positions of the absorption bands for the various solutions of the hydroxyhydroquinol and phloroglucinol compounds are listed in Table II.

Table II

Frequency Numbers of Bands in Solutions

		Hydroxyhydroquinolphthalein					
Absolute ethanol		2124	3055	3726	3804	4135	
Concd. sulfuric acid		2237	3195	3791	3900	4262	
Concd. potassium hydroxide	Fresh	1785	2715	2867	3342	3796	3923
	Faded		2775	2850	3350	3745	3930
		Hydroxyhydroquinolsulfonephthalein					
Absolute ethanol		2122	3082	3688	3781	4107	
Concd. sulfuric acid		2213	3160	3766	3847	4290	
Concd. potassium hydroxide	Fresh	1763	2709	2872	3343	3795	3928
	Faded		2710	2900	3400	3705	4000

TABLE II (*Concluded*)

Phloroglucinolsulfonephthalein

Absolute ethanol	2200		3177	3565	
Concd. sulfuric acid	2235	2781	3376	3564	3840
Concd. KOH, fresh	2047	3137	3425		

Both hydroxyhydroquinolphthalein and hydroxyhydroquinolsulfonephthalein behave in an unusual manner, when gradually increasing amounts of potassium hydroxide are added to their neutral absolute ethanol solutions. With most of the colored phthaleins and sulfonephthaleins, it has been observed that over a certain range of alkali concentrations there is a more or less rapid disappearance of the visual band of the neutral solution and a corresponding growth of the band characteristic of the alkaline solution.[15] The wave-length positions of the neutral and alkaline bands remain fixed, since they are due to the presence of two different substances, the neutral form and the basic form, and the relative intensities are a measure of their relative concentrations and therefore of the state of equilibrium between them.[16] In the case of the hydroxyhydroquinol derivatives, as illustrated in Fig. 7 by the set of curves covering the visual region for alkaline solutions of hydroxyhydroquinolphthalein, there is, however, an almost continuous shift of the bands toward the red, while the intensities pass through a maximum for an intermediate concentration of alkali. Curve A is a reproduction of the visual portion of the absorption

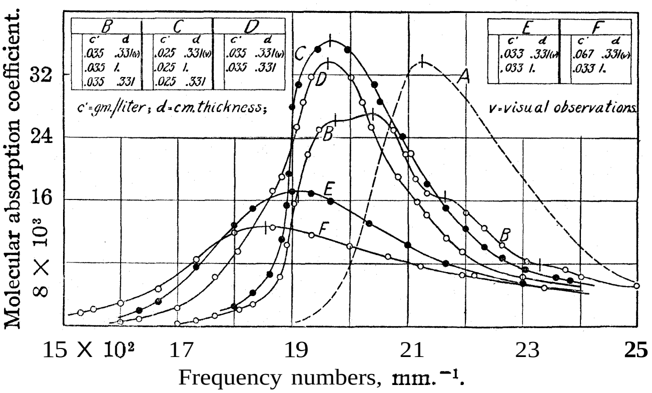


Fig. 7.—Hydroxyhydroquinolphthalein in alcoholic potassium hydroxide: A, neutral solution; B, 1 molecule:2 molecules of KOH; C, 1 molecule:4 molecules of KOH; D, 1 molecule:23 molecules of KOH; E, 1 molecule:87 molecules of KOH; F, 1 molecule:100 molecules of KOH.

---

[15] See references 3a, 3e, 4 and 5; also Brode, THIS JOURNAL, 46, 585 (1924), and Holmes, *ibid.*, 46, 629 (1924).

[16] Gibbs and Shapiro, Proc. Nat. *Acad. Sci.*, 14, 694 (1928).

curve for the neutral solution. Curve B for two molecules of potassium hydroxide to one of the phthalein has a lesser intensity and there are present a prominent double band and two weak shoulders in place of the single band of the neutral solution. For four and twenty-three molecules of alkali, Curves C and D, there are now present again only single bands but shifted to the region of frequency number 1990 while the maximum of intensity has been reached at Curve C. Thereafter further additions of alkali, 87 molecules for Curve E and 100 molecules for Curve F, produce a rapid shifting of the band toward the red together with a marked decrease of intensity. Coincident with these changes in absorption, there is first an increase and then a disappearance of fluorescence. The neutral solution shows faint fluorescence, but with the addition of alkali up to twenty-three molecules, this becomes quite intense, corresponding to the increased absorption at this concentration. Abruptly with the shift of the band from its position on Curve D to that of Curve E, the fluorescence completely disappears. If there are assumed several changes in molecular configuration during the addition of the potassium hydroxide and therefore a correspondingly complex set of equilibrium conditions, it is possible at least qualitatively to interpret the above data. It was demonstrated above that hydroxyhydroquinolphthalein in neutral ethanol solution possesses the structure of an inner salt. In the presence of an amount of alkali insufficient to form the tetrabasic salt, it is conceivable that the molecule would revert to the condition of the free acid, which would have a different type of absorption from that of the inner salt. It is therefore significant, inasmuch as hydroxyhydroquinolphthalein may be regarded as dihydroxyfluorescein, that Curve B for two molecules of potassium hydroxide, half the theoretical amount, closely resembles the curves for neutral solutions of resorcinolbenzein[4a] and fluorescein,[4b] both quinoid compounds and the latter a free acid. With four and twenty-three molecules, salt formation is completed and the fluorescence is at a maximum, but with more alkali a decisive change must be produced in the molecule, corresponding to the creation of a new type of absorption and the loss of the fluorescence. Since the hydroxyhydroquinolphthalein can be reprecipitated from the non-fluorescent solution by the addition of acid, this last change is reversible and hence must be in equilibrium with the other two processes—the rupture of the inner salt bond and the formation of the tetrabasic salt. The ultraviolet spectrum, which consists of three well-defined bands for the solution containing four molecules of potassium hydroxide, undergoes no unique changes such as are found in the visual region, but with increasing alkali concentrations the bands become shallower until in the presence of 100 molecules it is difficult to locate them with accuracy. For completeness all of the bands for the various alkaline solutions are listed in Table III.

TABLE III

FREQUENCY NUMBERS OF BANDS IN ALCOHOLIC ALKALINE SOLUTIONS OF HYDROXYHYDROQUINOLPHTHALEIN

Ratio to KOH							
1:2	1975	2039	2105	2330	3018	3657	4125
1:4	1965				2911	3612	4093
1:23	1962				2950	3600	4092
1:87	1911				2995	3558	3987
1:100	1855				2900	3450	3950

Summary

1. Data and curves are presented on the absorption spectra of various phthalein derivatives of pyrogallol, hydroxyhydroquinol and phloroglucinol. Correlations are drawn with data previously obtained for phthaleins of the mono- and dihydroxybenzenes.

2. The effect on the chemical properties and absorption spectra of the phthaleins, due to the introduction of hydroxyl groups, is discussed.

3. Gallein, which is colored in both the solid state and in neutral solution, is shown to be primarily lactoid in structure, but probably in equilibrium with a small amount of the quinoid modification.

4. The unusual behavior of hydroxyhydroquinolphthalein in weakly alkaline solutions both as regards its absorption and fluorescence is described and a possible explanation is advanced.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

THE PREPARATION OF AMINONAPHTHOLS

BY WILSON F. BROWN, JOHN C. HEBDEN AND JAMES R. WITHROW

RECEIVED SEPTEMBER 4, 1928 PUBLISHED JUNE 5, 1929

1-Amino-7-naphthol and 1-amino-6-naphthol were needed for work in progress. An investigation was therefore conducted for the preparation of these compounds by caustic fusion of the respective α-naphthylaminesulfonic acids.

Among other things, the results indicated that 1-amino-6-naphthol could be prepared from α-naphthylamine-6-sulfonic acid by caustic soda fusion. The melting point of the picrate of 1-amino-6-naphthol was not the same as that given in the literature. Further, 1-amino-7-naphthol was prepared in good yield (average of 58%) by caustic soda fusion of α-naphthylamine-7-sulfonic acid.

Literature

The Cassella Company[1] gave an example of the preparation of 1-amino-7-naphthol by caustic fusion from α-naphthylamine-7-sulfonic acid In

---

[1] German patent 69,458; *Friedländer*, 3, 476 (1890).

the first part an autoclave is used and in the second part an open kettle. They do not mention the 1-amino-6-naphthol.

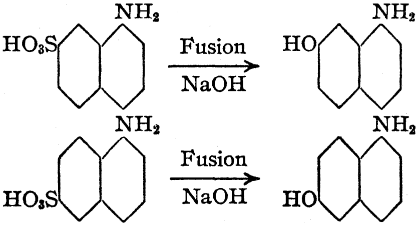
Kehrmann and Engelke[2] described the purification of crude 1-amino-7-naphthol and gave the melting point of the purified product as 205–207°. They also described the preparation of the mono-acetyl compound of 1-amino-7-naphthol.

1-Amino-6-naphthol was prepared by nitration of naphthalene, according to Friedländer,[3] and subsequent partial reduction.

Franz Sachs[4] gave a method for the production of 1-amino-6-naphthol in his patent on the preparation of aminonaphthols by the action of sodamide on naphthol sulfonic acids. He stated that the melting point of the 1-amino-&naphthol was 185°.

Nowhere in the literature was there found a process for the preparation of 1-amino-6-naphthol by fusion of a-naphthylamine-6-sulfonic acid with caustic soda. A method was devised, therefore, based on the illustration of the Cassella patent for the 1,7-compound.

The reactions involved in the preparation of the 1-amino-7-naphthol and 1-amino-6-naphthol were anticipated to be the following



Experimental

Preparation of **Aminonaphthols.**—The Cassella illustration for the 1,7-compound was investigated but failed to work. When the temperature of the fusion was raised from 265 to 305°, however, good results were obtained. The method finally adopted consisted in melting caustic soda, with the addition of a small quantity of water, and then adding the a-naphthylaminesulfonic acid gradually to avoid foaming. When all of the α-naphthylaminesulfonic acid was in, the melt was heated to 265–275° for one hour, then to 305° for five minutes and finally cooled to 200°. The aminonaphthol was isolated by diluting the melt with water, neutralizing with hydrochloric acid, boiling, filtering and adding soda solution until no more precipitation could be obtained.

Preparation of 1-Amino-6-Naphthol.—In preparing to make the 1-amino-6-naphthol the method selected was that given by the Cassella Company[1] for making 1-amino-7-naphthol. This method was followed as to proportions but here also it was found necessary to heat to approximately 305° in order to complete the reaction when an open pot was used. The isolation of the final product presented no difficulties. The yield of 1-amino-6-naphthol was consistently good and even better than the 1,7. There was some loss of aminonaphthol, however, by volatilization.

---

[2] Kehrmann and Engelke, *Ber.,* 42,351 (1909).

[3] Friedlander, *Ber.,* 25,2079 (1892); 29,1979 (1896); 39,3016 (1906).

[4] German patent 173,522; *Friedländer,* 8, 172 (1905–1907).

Acetylation of 1-Amino-6-naphthol.—The method of Kehrmann and Engelke[5] for the preparation of the acetyl compound of 1-amino-7-naphthol was followed in attempting to prepare the acetyl compound of 1-amino-6-naphthol. One part of 1-amino-6-naphthol was mixed with three parts of acetic anhydride, the mixture becoming slightly warm. It was warmed on the hot-plate for a few minutes, filtered and the mass washed with water. The residue was extracted with boiling dilute ethyl alcohol (1:1) and filtered. The filtrate was allowed to cool and the precipitate that came out was filtered and dried in air. On testing, the substance melted gradually, starting at 195" and continuing up to 220°. The mono-acetyl and di-acetyl compounds are said to melt at 218 and 186°, respectively.[6]

TABLE I

1-AMINO-7-NAPHTHOL

Experiment no.	27	28	32	91	92	93	94	95
Sulfonic acid used, g.	20	40	40	252	252	252	252	252
Yield of base, g.	7.3	5.0	12.0	71.0	42.0	58.0	144.0	76.0
Yield of hydrochloride, g.	..	..	..	38.0	95.0	78.0	...	...
Yield calcd. as base, g.	..	..	..	101.9	119.3	121.4	...	...
Yield based on sulfonic, %	51.2	17.5	42.0	56.7	66.3	67.6	80.1	42.3

Variation in yield due mainly to volatilization of aminonaphthol from open pot.

TABLE II

1-AMINO-6-NAPHTHOL

Experiment no.	29	30	33	67	68	69	70	96	97
Sulfonic acid used, g.	40	40	40	252	252	252	252	252	252
Yield of base, g.	24.4	20.2	22.7	151.0	58.0	96.0	42.0	105.0	53.0
Yield of hydrochloride, g.	..	..	..	...	...	...	...	57.0	116.0
Yield calcd. as base, g.	..	..	..	...	...	...	...	151.4	147.4
Yield based on sulfonic, g.	85.6	70.8	79.6	84.0	32.3	53.4	23.4	84.2	82.0

Variation in yield due mainly to volatilization of aminonaphthol from open pot.

Purification of 1-Amino-6-Naphthol.—The 1-amino-6-naphthol was purified in two ways. (A) The 1-amino-6-naphthol was extracted with 7.5% hydrochloric acid, filtered and ammonium hydroxide added to the filtrate just to alkalinity. Three crops of precipitates were obtained, the third of which was crystalline and gave a melting point of 186.8°, corrected. (B) The 1-amino-6-naphthol was purified by repeated recrystallization from boiling water. The melting point of the purified product was found to be 190.6" corrected. As previously mentioned, Sachs gave the melting point as 185" but did not state whether it was corrected or not.

Identification of 1-Amino-6-Naphthol.—The picrate of 1-amino-6-naphthol was prepared several times and a melting point of 170°, corrected, obtained. This is not in accord with the value given by Sachs,[4] who states that the picrate of 5,2-aminonaphthol (1-amino-6-naphthol) melts at 185° (as he states for the parent substance also). The hydrochloride was prepared by adding an excess of hydrochloric acid to the melt during neutralization and cooling the solution to room temperature. The 1-amino-6-naphthol hydrochloride separated in glistening, dark red crystals, whereas the hydrochloride of 1-amino-7-naphthol is gray. References to these two hydrochlorides are not found in the literature.

---

[5] Ref. 2, p. 351.

[6] German patent 173,522; *Friedländer*, 8, 172 (1905–1907).

Conclusions

1. The I-amino-7-naphthol was prepared in good yield and of good quality from α-naphthylamine-7-sulfonic acid by caustic soda fusion, at much higher temperatures than were given by Cassella and was isolated both as the base and as the hydrochloride.

2. The 1-amino-6-naphthol was prepared in good yield and of good quality from α-naphthylamine-6-sulfonic acid, by caustic soda fusion, and was isolated both as the base and as the hydrochloride.

3. Acetylation of the I-amino-6-naphthol was unsuccessful.

4. The melting point of the picrate of 1-amino-6-naphthol was found to be 170°, corrected, as against 185° as given by Sachs.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SOME HALOGENATED FLUORESCEINS[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

RECEIVED SEPTEMBER 6, 1928 PUBLISHED JUNE 5, 1929

In previous investigations on the absorption spectra of resorcinolbenzein,[3a] fluorescein[3b] and sulfonefluorescein[3'] in various solvents, the effect of introducing acid groups, carboxyl and sulfoxyl, into the benzein was studied. It was shown that in the presence of the highly dissociated sulfonic acid group an inner salt was formed with the basic, quinoid oxygen atom. Dibromosulfonefluorescein[3'] also exhibited the inner salt configuration, but the bands in its absorption spectra were shifted toward longer wave lengths relative to those of sulfonefluorescein, as the result of the addition of two bromine atoms.

Data are now presented for di- and tetrabromofluorescein (eosin), in which the bromine atoms are attached to the phenol residues, and for tetrachlorofluorescein, in which the chlorine replaces the hydrogen atoms of the phthalic acid residue. It is known from the work of B. Cohen[4] on indicators of the sulfonephthalein class that halogen substitution in the phenolic residues results in an increase in the apparent dissociation constant of the phenolic hydrions. Although his data on the halogen derivatives give

---

[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

[3] (a) Orndorff, Gibbs and Shapiro, THIS JOURNAL, 48, 1327 (1926); (b) *ibid.*, **50,** 819 (1928); (c) Gibbs and Shapiro, *ibid.*, **50,** 1755 (1928).

[4] B. Cohen, *Public Health* ***Reports,*** *41,* 3053 (1926).

no indication of a similar effect on the dissociation of the acid group, carboxyl or sulfoxyl, such an effect is nevertheless to be expected, since it has been shown that the properties of the acid group, as well as the hydroxyl, are modified by alkyl[4] and hydroxyl[5] substitutions. In order that a change in the acid properties shall be recognizable from a study of absorption spectra, it is necessary in the case of fluorescein, which exists as a free acid in the quinoid state, that substitution shall either increase the acid properties to such an extent that an inner salt is formed, or decrease them to a point where the lactone becomes stable. In the first case the absorption spectra of the neutral and acid solutions will be found to be similar;[5] in the second case, the neutral solutions will show the characteristic absorption bands of the benzenoid phthaleins.[6] The results of the present investigation bring out, however, a complete similarity between the absorption spectra of fluorescein and its halogen derivatives and indicate that any changes in the acid properties are relatively slight and are negligible compared with the effects produced by the introduction of hydroxyl groups. In other words, whatever effect there may be upon the acidity, it is not sufficient to produce marked changes in the absorption spectra. The result of halogen substitution is primarily to shift the absorption bands toward longer wave lengths, with the most pronounced changes occurring for eosin and the least usually for tetrachlorofluorescein. Dibromofluorescein, which has about the same molecular weight as the tetrachloro compound but differs from it in having the bromine atoms on the phenol residues, shows shifts in its absorption bands intermediate between those of eosin and tetrachlorofluorescein. It thus appears that substitution in the phenol residues is more effective than substitution in the phthalic acid portion of the molecule in modifying the absorption of fluorescein.

The compounds used in the present investigation were all of analytical purity.[7] The sample of eosin[7b] was almost white in color but its solution in absolute ethanol did not differ from that of another pure sample which was a deep pink in the solid state. It must therefore be assumed, as with the red and yellow varieties of fluorescein,[3b] that if any differences in structure exist in the solid state they disappear when in solution, probably by giving rise to an equilibrium mixture of the lactoid and quinoid forms, in which the latter predominates.

Figure 1 presents the absorption curves for absolute ethanol solutions of dibromo-, Curve A,A′, tetrabromo-, Curve B,B′ and tetrachlorofluorescein, Curve C,C′. The absorption curve for fluorescein, Curve D,D′, is repeated from our previous paper,[3b] where data on the concentrations em-

---

[5] Gibbs and Shapiro, THIS JOURNAL, 51, 1755 (1929).

[6] Gibbs and Shapiro, *Proc. Nat. Acad. Sci.*, *14*, 251 (1928).

[7] (a) Orndorff and Hitch, THIS JOURNAL, *36*, 680 (1914); (b) Orndorff and Hemmer, *ibid.*, *49*, 1272 (1927).

ployed will be found. The positional effect of the halogen atoms is most marked in the visual and near ultraviolet regions, where the absorption of eosin is nearly eight times as intense as that of tetrachlorofluorescein or of fluorescein itself and its bands are shifted to the greatest extent. In the ultraviolet region eosin again exhibits the greatest intensity, but tetrachlorofluorescein now lies intermediate between it and dibromofluorescein.

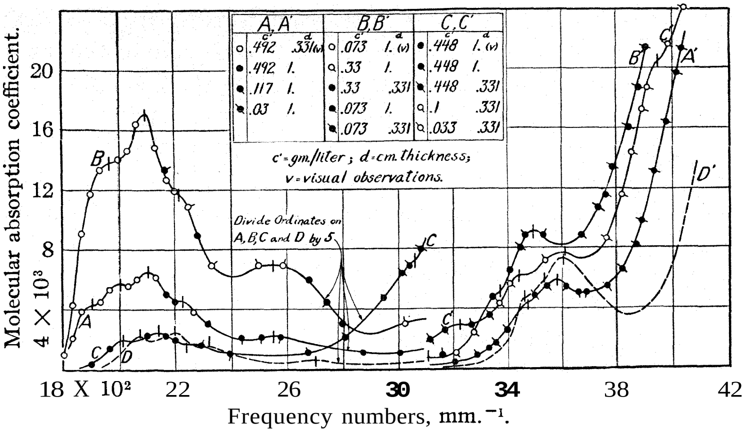


Fig. 1.—Neutral ethanol solutions: A,A', dibromofluorescein; B,B', tetrabromofluorescein–eosin; C,C', tetrachlorofluorescein; D,D', fluorescein.

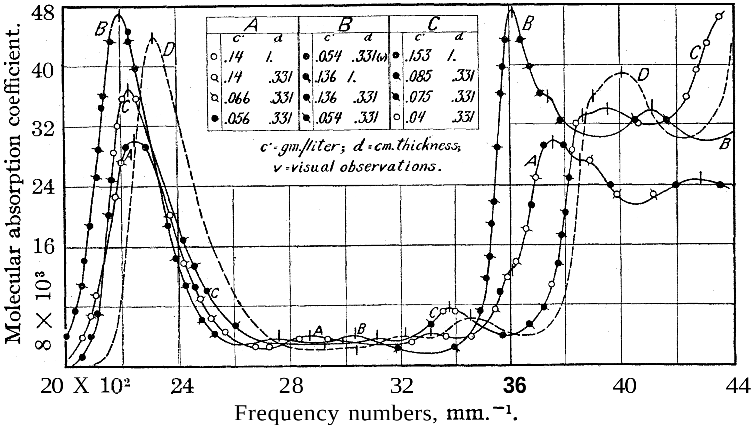


Fig. 2.—Concd. sulfuric acid solutions: **A**, dibromofluorescein; B, tetrabromofluorescein–eosin; ***C***, tetrachlorofluorescein; D, fluorescein.

The mass effect of halogens is brought out in the extreme ultraviolet range by the fact that the rapid increase of absorption occurs at relatively longer wave lengths for Curves A' and B' as compared with Curve D'.

The absorption curves of the sulfuric acid solutions are given in Fig. 2.

The lack of any resemblance of these curves to those obtained for the neutral solutions, Fig. 1, is evidence for the non-existence of an inner salt structure for the halogenated fluoresceins. This is confirmed by the finding that fluorescein and dibromofluorescein form hydrochlorides; eosin also adds on dry hydrogen chloride but less readily than the above compounds.[7b] According to Orndorff and Hitch,[7a] tetrachlorofluorescein does not form a hydrochloride under any circumstances, but in this respect it is probably similar to phenolphthalein, whose hydrochloride is stable only at −30°.[8] Orndorff and Hitch ascribe the failure to obtain a hydrochloride to the weakly basic properties of the quinoid oxygen atom but it is evident by analogy with fluorescein that a sulfate is formed in concd. sulfuric acid. The visual band for the halogenated compounds is shifted markedly toward the red from that of fluorescein in the following order: tetrabromo > tetrachloro > dibromo. The order of these shifts, as well as their magnitude, agrees closely with the results obtained by Holmes[9] for the same compounds in weakly alkaline solutions. In the ultraviolet, however, tetrachlorofluorescein is relatively close to fluorescein, while the two dibromo derivatives exhibit a large shift toward the red. Another striking difference between these two groups is in the relative intensities of the two components of the complex ultraviolet band. For the first pair of compounds the short wave-length component is slightly the more intense, while for the second pair the long wave-length component is very much more intense. This complex band has been found to be characteristic of the sulfuric acid solutions of almost all phthaleins containing the pyrone ring and in the majority of cases its contour is of the second type. In the following list, Col. A represents those compounds for which the short wave-length component is the stronger and Col. B those for which it is the weaker.

A	B	
Fluorescein	Dibromofluorescein	Tetrabromofluorescein
Tetrachlorofluorescein	Sulfonefluorescein[3c]	Sulfonegallein[6]
Hydroxyhydroquinolphthalein[5]	Dibromosulfonefluorescein[3c]	Gallein[5]
Hydroxyhydroquinolsulfonephthalein[5]	Resorcinolbenzein[5]	Pyrogallolbenzein[5]

In ethanol solutions of these fluorescein compounds involving complex equilibrium conditions between several forms, it is not possible to isolate completely the effect of halogen substitution, whereas in concd. sulfuric acid solution we may safely assume the existence of these several compounds in analogous states and may therefore ascribe the differences in their absorption more definitely to halogen substitution. Halogenation of the phenolic groups thus appears to bring two opposing forces into action: (1) a tendency to decrease the intensity which can be ascribed to the intrinsic nature of the halogen; (2) a tendency to increase the intensity,

---

[8] Meyer and Hantzsch, *Ber.*, 40, 3479 (1907).

[9] Holmes, THIS JOURNAL, 46, 2770 (1924).

which may be ascribed to the mass action of the halogen. It should be possible to judge the relative importance of these two factors by a study of derivatives of fluorescein in which bromine is replaced by chlorine or iodine.

The positions of the absorption bands for the neutral and acid solutions of fluorescein and its halogenated derivatives are listed in Table I.

TABLE I

FREQUENCY NUMBERS OF BANDS FOR NEUTRAL AND ACID SOLUTIONS OF HALOGENATED FLUORESCEINS

Fluoresceins				Fluoresceins			
Fluorescein	Dibromo-	Tetrabromo- (eosin)	Tetrachloro-	Fluorescein	Dibromo-	Tetrabromo- (eosin)	Tetrachloro-
Absolute Ethanol as Solvent				Concd. Sulfuric Acid as Solvent			
	1905						
2075	2005	1968	2013	2317	2250	2201	2228
2198	2106	2100	2141	3039	2868	2759	2922
2319	2227	2215	2239	3215	2987	3032	3111
2700	2548	2548	3060	3451	3307		3377
3460		3107	3224		3605		
3533	3472	3371	3441	3906	3755	3605	3868
3604	3580	3492	3610	4005	3857	3738	3957
			3949		4287	4115	

Summary

1. The effects of halogen substitution on the absorption spectra and chemical properties of fluorescein are discussed. Absorption curves and data are presented for dibromo-, tetrabromo- and tetrachlorofluorescein.

ITHACA, NEW YORK

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

ETHYL- AND HEXYLFLUORESCEIN. THEIR DIBROMO AND MONOMERCURY DERIVATIVES

BY REUBEN B. SANDIN AND JOHN W. SUTHERLAND

RECEIVED DECEMBER 26, 1928 PUBLISHED JUNE 5, 1929

A great number of mercury derivatives of phenolphthalein and related compounds has been prepared. Many of these have been reported in the patent literature.[1] White[2] has prepared mercury derivatives of phenolphthalein, o-cresolphthalein, fluorescein, dibromofluorescein and phenolsulfonephthalein, containing from one to four atoms of the metal. Very recently Harden[3] has reported salicylsulfonephthalein, its tetrabromo and monomercury derivatives. The latter compound shows marked germicidal power.

[1] Pauly and Traumann, German Patent 201,903 (1909); Fahlberg, List and Co., German Patent, 308,335 (1918); White, U. S. Patent 1,535,003 (1925); 1,549,942 (1925).

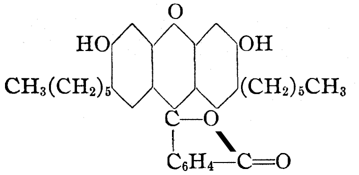
[2] White, THIS JOURNAL, 42, 2355 (1920).

[3] Harden, *ibid.*, 49, 3139 (1927).

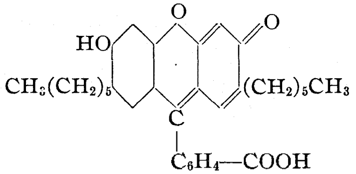
In connection with a study of the mercuration of the alkylresorcinols,[4] the authors have prepared the monomercury and dibromo derivatives of ethyl- and hexylfluorescein. At present work is proceeding on a study of the bactericidal value of the mercury derivatives.

The ethyl- and hexylfluoresceins were prepared by the action of phthalic anhydride on ethyl- and hexylresorcinol,[5] respectively. This was done in a manner similar to Gatterman's[6] preparation of fluorescein, with the exception that the cold melt was extracted with a solution of sodium hydroxide and the dye then precipitated by the addition of hydrochloric acid or acetic acid.

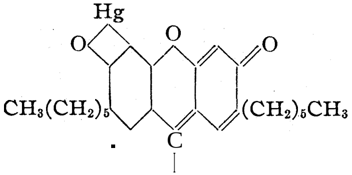
In the preparation of the ethyl- and hexylfluorescein, some observations have been made which are similar to the observations made by Orndorff and Hemmer[7] in connection with fluorescein. When an alkaline solution of ethyl- or hexylfluorescein, as obtained in the original preparation, was treated with acetic acid in the cold, the yellow dye was precipitated. However, when a boiling alkaline solution of either phthalein was treated with concentrated hydrochloric acid, the dye in each case was precipitated as a dark brown amorphous mass. In accordance with the views of Orndorff and Hemmer, a suggested structure for the yellow modification is Formula I, and for the brown modification, Formula II.



I. Yellow hexylfluorescein (lactoid)



II. Brown hexylfluorescein (p-quinoid)



III. Anhydromonomercurihexylfluorescein

The dibromo compounds were prepared in the usual way by the addition of a slight excess over the required two moles of bromine to a suspension or solution of one mole of the phthalein in glacial acetic acid. The mono-

---

[4] Sandin, THIS JOURNAL, 51,479 (1929).

[5] The ethylresorcinol used was prepared according to Johnson and Hodge, *ibid.*, 35, 1014 (1913). The hexylresorcinol was prepared according to Dohme, Cox and Miller, *ibid*, 48, 1688 (1926).

[6] Gatterman, "The Practical Methods of Organic Chemistry," Macmillan Co., New York, 1921, p. 357.

[7] Orndorff and Hemmer, THIS JOURNAL, 49,1272 (1927).

mercury compounds were formed by the addition of a solution of one mole of mercuric acetate in hot alcohol and acetic acid to one mole of the dye dissolved in hot alcohol. A suggested structure for the monomercury compounds is shown by Formula III.

The results of the experiments are collected in the following tables.

TABLE I

PROPERTIES AND ANALYSES OF VARIOUS MODIFICATIONS OF ETHYL- AND HEXYL-FLUORESCEIN

Color of powder	Obtained by	Analyses, found, % C		H	
Ethylfluorescein, $C_{24}H_{20}O_5$. Calcd.: C, 74.22; H, 5.15					
Dark brown	Adding HCl to hot NaOH soln.	73.98		5.02	
Yellow	Adding AcOH to cold NaOH soln.	73.93		5 21	
Dark brown	Boiling with HCl	7394	73.85	5.03	5.07
Brown[a]	Slow evap. of alc. soln.	73 93		5.02	
Hexylfluorescein, $C_{32}H_{36}O_5$. Calcd.: C, 76.80; H, 7.20					
Brown	HCl to boiling NaOH soln.	76.41		7.12	
Yellow	AcOH to cold NaOH soln.	76.73		7.15	

[a] On pulverizing; crystals with greenish-purple surface color.

TABLE II

PROPERTIES AND ANALYSES OF THE DIBROMO DERIVATIVES OF ETHYL- AND HEXYL-FLUORESCEIN

Dibromo-( )-fluorescein	Formula	Color of powder	M. p., °C.	Br, Analyses, % Calcd.	Found	
Ethyl	$C_{24}H_{18}O_5Br_2$	Reddish-brown	Does not melt at 300°	29.27	29.03	29.10
Hexyl	$C_{32}H_{34}O_5Br_2$	Reddish-brown	180–181°	24.29	24.04	24.09

TABLE III

PROPERTIES AND ANALYSES OF THE MONOMERCURY DERIVATIVES OF ETHYL- AND HEXYLFLUORESCEIN

Anhydromonomercuri-( )-fluorescein	Formula	Color of powder	Calcd., % Hg	Acetic acid	Found, % Hg			Acetic acid
Ethyl	$C_{24}H_{18}O_5Hg$	Red	34.19	0	33.60	34.09	33.90	0
Hexyl	$C_{32}H_{34}O_5Hg$	Red-brown	28.71	0	28.27	28.44	28.34	0

Summary

1. The preparation of ethyl- and hexylfluorescein and their dibromo and monomercury derivatives has been described.

2. Ethyl- and hexylfluorescein each exists in two isomeric forms, a yellow and a brown. The formula of the two isomeric ethylfluoresceins is $C_{24}H_{20}O_5$, and of the two isomeric hexylfluoresceins is $C_{32}H_{36}O_5$. The yellow form is prepared by adding acetic acid to a cold alkaline solution of the dye, and according to Orndorff and Hemmer is given the lactoid structure. The brown modification is obtained by adding hydrochloric acid to a boiling alkaline solution of the dye. It is given the p-quinoid structure.

EDMONTON, ALBERTA, CANADA

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

THE ACTION OF BROMINE ON CERTAIN MIXED ETHERS

By L. Chas. Raiford and D. M. Birosel

Received December 29, 1928 Published June 5, 1929

Henry[1] obtained phenyl allyl ether by the action of allyl bromide on sodium phenolate, but gave no details regarding the method and recorded no yield. He noted that when bromine was brought in contact with the ether, both the allyl and the phenyl radicals reacted. However, nothing was said about the character of the product. 2,4,6-Tribromophenyl allyl ether was obtained by Varda[2] by the alkylation of the bromophenol, and Claisen and Eisleb[3] obtained 4-bromophenyl allyl ether by synthesis from *p*-bromophenol, not by bromination of the ether. Fairbourne and Toms[4] brominated 2,4-dinitrophenyl allyl ether and, as might have been predicted,[5] found that the halogen entered the allyl radical only. Colbert,[6] working in this Laboratory, noted similar behavior with 2-nitro-4-chlorophenyl allyl ether, though the amount of material available and the difficulty of purification prevented absolute identification of the product. In view of these facts, it was proposed to test the action of bromine on phenyl allyl ether under conditions where both radicals might react.

When phenyl allyl ether was treated with excess[7] of bromine it gave some 2,4,6-tribromophenol and a tetrabromo ether. The identity of the ether was established by preparing it in a different way. 2,4-Dibromophenol was converted into the corresponding allyl ether and the latter was treated with excess of bromine. The tetrabromo ether isolated in the first experiment was obtained here.

The failure to introduce more than two atoms of bromine into the phenyl radical of phenyl allyl ether under the conditions stated suggested the examination of ethers containing alkyl radicals. The methyl, ethyl and propyl ethers of 2,4,6-tribromophenol are on record, but only the

---

[1] Henry, *Ber.*, **5**, 455 (1872).

[2] Varda, *Gazz. chim. ital.*, [2] **23**, 495 (1893).

[3] Claisen and Eisleb, *Ann.*, **401**, 38 (1913).

[4] Fairbourne and Toms, *J. Chem. Soc.*, **119**, 1038 (1921).

[5] It is well known that the difficulty of introducing substituents into the phenyl radical increases as the number of groups present increases, and that the ether or ester is less reactive than the corresponding phenol. This relation was emphasized in the preparation of the bromine addition product of *o*-allyl phenol by Adams and Rindfusz, This Journal, **41**, 654 (1919), who found it necessary to protect the hydroxyl group by acetyl, to use only the calculated amount of bromine to saturate the allyl radical and to conduct the experiment at 0°.

[6] Colbert, unpublished report.

[7] More than that required to saturate the allyl radical and to substitute positions 2,4 and 6 in the phenyl group.

first was made by bromination of the ether. In the present work, in which the ethers were allowed to remain in contact with excess of bromine for several days, it was found that, in addition to bromination of the phenyl radical, certain ethers were split by the hydrogen bromide formed. With phenyl methyl, ethyl, n-propyl and isobutyl ethers, the 2,4,6-tribromo ether[8] resulted; with 2,4,6-tribromophenyl n-propyl and isopropyl, no changes occurred, while with phenyl isopropyl, *sec.*-butyl[9] and *tert.*-butyl, and with 2,4-dibromophenyl isopropyl and to the extent of 10 and 20%, respectively, with phenyl methyl and ethyl, the 2,4,6-tribromophenol[10] was formed.

Experimental Part

A. Phenyl Allyl Ether and Substitution Products

2,4-Dibromophenyl-β,γ-dibromopropyl Ether.—Twelve g. of phenyl allyl ether[11] dissolved in 10 cc. of chloroform was treated gradually with an excess of bromine in chloroform, with cooling, the mixture allowed to stand for four days and then the solvent and excess of bromine were distilled off. Distillation under reduced pressure gave one fraction that boiled just below 190° at 5 mm. and which solidified upon standing. Crystallization from petroleum ether gave nearly colorless needles that melted at 93°[12] A second fraction distilled at 220–223° at 10 mm., apparently with slight decomposition. This did not solidify on standing. Analysis is given in Table I.

2,4-Dibromophenyl Allyl Ether.—This was obtained in 54% yield by converting 25 g. of the corresponding dibromophenol into the ether by Claisen's general method. The product distilled between 165 and 170° at 20–22 mm and was nearly colorless. It did not solidify upon cooling. When a chloroform solution of this product was treated with an excess of bromine, it gave the tetrabromo compound described above.

2,4,6-Tribromophenyl-β,γ-dibromopropyl Ether.—Twenty-eight g. of *s*-tribromophenyl allyl ether, m. p.[13] 75°, was dissolved in 100 cc. of chloroform, 15 g. of bromine was added slowly with cooling and the mixture allowed to stand for three days, after which the solvent and excess of bromine were distilled off under reduced pressure.

---

[8] The ethyl derivative melted at 69° and is probably identical with that obtained by Purgotti [*Gazz. chim. ital.*, 16,528 (1886)] by treatment of the silver salt of the bromophenol with ethyl iodide, and who reported 69°, but did not analyze the product. Varda [*ibid.*, [II]23, 494 (1893)] used the potassium salt of the phenol and reported 72–73" for a substance that analyzed well, The product here in question was nearly pure. *Anal.* Subs., 0.1173: AgBr, 0.1840. Calcd. for $C_8H_7OBr_3$: Br, 66.83. Found: Br, 66.68.

[9] The product boiling between 100 and 108° under 40-mm. pressure, and obtained in 23% yield from phenol and secondary butyl bromide by Claisen's method, was used.

[10] Sodium acetate in the reaction mixture prevents splitting except in the case of phenyl *tert.*-butyl ether.

[11] Claisen and Eisleb, *Ann.*, 401, 29 (1913).

[12] Repetition of this experiment showed that this fraction consisted mainly of 2,4,6-tribromophenol. The hydrogen bromide evolved in the conversion of a portion of this ether into a bromine substitution product decomposed some of it to give phenol, which was then brominated. If the bromination is conducted in the presence of sodium acetate, the splitting and consequent formation of tribromophenol can be avoided.

[13] Varda, ref. 2, recorded 77°.

Recrystallization from ligroin (40–60°) by cooling in a freezing mixture gave nearly colorless needles.

2-Nitro-4-chlorophenyl-8,r-dibromopropyl Ether.--One g. of the corresponding **nitrochlorophenyl** allyl ether'' was treated with excess of bromine in chloroform solution and allowed to stand for a few days After removal of solvent and excess of bromine, the oily residue was held at about 98° and 20 mm. for several hours and then allowed to cool and solidify. Crystallization from petroleum ether gave colorless needles.

2,4,6-Trinitrophenyl-β,γ-dibromopropyl Ether.—Five g. of picryl allyl ether[15] was dissolved in chloroform, an excess of bromine in the same solvent added and the mixture allowed to stand for twenty-four hours. Evaporation of solvent and unchanged bromine left a colored solid which after repeated crystallization from petroleum ether gave nearly colorless prisms.

B. Phenyl Alkyl Ethers

2,4-Dibromophenyl Isopropyl Ether.—This was prepared by Claisen's method from the dibromophenol and isopropyl iodide, and was obtained as an oil that distilled at 156° and 18 mm.

2,4,6-Tribromophenyl Isopropyl Ether.—This was obtained in 74% yield from tribromophenol with a slight excess of isopropyl bromide. At 190° and 30 mm. it distilled as a faintly colored oil that solidified on standing.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound β,γ-Dibromopropyl ethers	Formula	M. p., °C.	Analyses, %		
				Calcd.	Found
2,4-Dibromophenyl-	$C_9H_8OBr_4$	Liq.	Br	70 75	70.80
2,4,6-Tribromophenyl-	$C_9H_7OBr_5$	42.5–435	Br	75.32	75.23
2-Nitro-4-chlorophenyl-	$C_9H_8O_3NClBr_2$	55	Hal	52 32	52.31
2,4,6-Trinitrophenyl-	$C_9H_7O_7N_3Br_2$	102[a]	Br	37 27	37 23
Isopropyl ethers					
2,4-Dibromophenyl-	$C_9H_{10}OBr_2$	Liq.	Br	54.42	54.37
2,4,6-Tribromophenyl-	$C_9H_9OBr_3$	40	Br	64.34	64.26

[a] After this work had been completed Fairbourne and Foster [J. *Chem. Soc.*, 3148 (1926)], published a report in which this product was assigned a melting point of 106–107°, while the allyl ether from which it was obtained melted at 90°.

Summary

1. Under the conditions of these experiments only two bromine atoms were introduced into the phenyl radical of phenyl allyl ether.

2. The hydrogen bromide evolved in 'the bromination of the ethers tested may split them unless sodium acetate is present. The splitting is most pronounced when the alkyl is connected through a secondary or tertiary carbon atom.

3. Further work on these derivatives is in progress.

IOWA CITY, IOWA

---

[14] Raiford and Colbert, THIS JOURNAL, **48,** 2658 (1926).

[15] Attempts to prepare this product by Claisen's [Ann., **401,** 29 (1913)] and by Willgerodt's [*Ber.*, **12,** 765 (1879)] methods, respectively, were unsuccessful. Treatment of silver picrate with allyl bromide also failed, but substitution of the iodide gave the desired result. Extraction of the reaction mixture with petroleum ether gave a red oil which upon the addition of a little water gave a crystalline solid; m. p. 85°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CVII. THE EXAMINATION OF YEAST 'NUCLEIC ACID FOR 5-METHYLCYTOSINE[1]

BY TREAT B. JOHNSON AND HENRY H. HARKINS[2]

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

In a paper from this Laboratory on pyrimidines (CV) the authors[3] described the acetol test for thymine and 5-methylcytosine, II, which is applicable in the presence of the pyrimidines, uracil and cytosine, I. A technique was described which permits of the identification of any one of these four pyrimidines in the presence of another. The specific color test (acetol test) recommended for identifying thymine is so delicate that quantities of this pyrimidine as small as one milligram can be detected with ease. The successful application of this acetol test for thymine and methylcytosine adds a new and practical procedure to our present technique for analysis of the pyrimidine content of a nucleic acid molecule.

The program outlined for research in this Laboratory on the "Chemistry of Bacteria" includes a study of the nature of the sugars linked in the nucleic acid of this bacterial cell. This work calls for a large supply of bacteria, but it is finally becoming possible through cooperation with commercial organizations to obtain bacteria, grown on synthetic media, in sufficient quantity to inaugurate an exhaustive study of the respective nucleic acids functioning in different types of bacterial cells. In the present stage of development of nucleic acid chemistry we have practically no knowledge of the composition of nucleic acids of bacterial origin. What accurate data we have regarding nucleic acid has been obtained by a study of a limited number of nucleic acids of animal origin and the nucleic acid of the yeast cell. The recent: results of biological experiments organized to include the study of the fundamental organic fractions of bacterial cells, as human, bovine and avian tubercle bacilli, indicate that the nucleic acid units of these cells play a significant and very important part in the life history of these lower organisms.

In the thymus nucleic acid molecule, and also in the nucleic acid of yeast, there is now no doubt as to the nature of the purine groupings which function as primary constituents. With reference to the pyrimidine constituents some doubt has been raised as to whether thymine and uracil are primary products, or whether they are hydrolytic products of methylcytosine, II, and cytosine, I, respectively. Present experimental evidence

---

[1] Constructed from a dissertation presented by Henry Harvey Harkins, in June, 1927, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

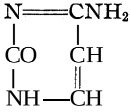
[2] Holder of the DuPont Fellowship in Chemistry.

[3] Harkins and Johnson, THIS JOURNAL, 51, 1237 (1929).

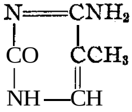
points to the conclusion that both uracil and cytosine function independently in the yeast nucleic acid molecule.

Of the nucleic acids of bacterial origin the one present in human tubercle bacilli—*tuberculinic* acid—has received the most attention. Johnson and Brown[4] made a careful examination of this substance, and they came to the conclusion that it is of the type of animal nucleic acids, that is, it contains a hexose sugar, cytosine and thymine, but no uracil. Later Johnson and Coghill continued the study of this interesting acid and obtained experimental evidence indicating that the cytosine fraction of tuberculinic acid contains a small amount of the pyrimidine 5-methylcytosine,[5] II. This was the first time that the natural occurrence of this aminopyrimidine has been observed. Johnson and Coghill identified the pyrimidine, II, as its picrate, by means of the characteristic crystallographic properties of this salt. The occurrence of this pyrimidine base in nature suggests again the possibility that the primary group in the thymine series may be 5-methylcytosine, and not thymine, in tuberculinic acid and also thymus nucleic acid. It is also possible that, while thymine is a primary constituent, 5-methylcytosine may be present in small amounts, and actually in an organic combination not to be accounted for by the present, proposed structure of thymus nucleic acid. If this last postulation be true, it might be expected that yeast nucleic acid may also actually contain a small amount of 5-methylcytosine.

I



II



In the light of this speculation, it seemed very desirable, therefore, to apply the most delicate tests available for detecting small amounts of 5-methylcytosine, II, in the presence of relatively large amounts of cytosine obtained from natural sources. The test for thymine and 5-methylcytosine which we have described in our previous paper (acetol test) can be applied successfully for detecting 5-methylcytosine under such conditions. Its application has also enabled us to decide in a new way quite conclusively whether 5-methylcytosine occurs mixed with cytosine in the nucleic acid of yeast.

When tuberculinic acids are available from new growths of tubercle bacilli of human, bovine and avian types, an exhaustive examination for all pyrimidines occurring in these bacteria will be made in this Laboratory.

The Preparation of Yeast Nucleic Acid.—Although there are many methods described in the literature for the preparation and purification of

---

[4] Johnson and Brown, *J. Biol. Chem.*, 54, 721 (1923); 57, 199 (1923); *see* also *Am. Rev. Tuberculosis,* 7, June, 1928.

[5] Johnson and Coghill, THIS JOURNAL, 47, 2838 (1925).

yeast nucleic acid, it is very difficult to obtain a product which does not give a biuret reaction. Nearly all of these methods are modifications of one proposed by Altmann in 1889.[6] The most important improvements in technique have been recommended by Baumann,[7] Levene and La Forge[8] and also Steudel.[9] The latter investigator examined carefully the action of alkali on yeast nucleic acid and he pointed out the fact that 5% sodium hydroxide solution at room temperature causes nucleic acid to split off guanine-nucleotide. If the temperature is hold at 0°, however, no decomposition results. Steudel, therefore, extracted the yeast cell with 5% sodium hydroxide and kept the temperature at or below 0°. In this way he obtained a product which was protein free and which gave good values for nitrogen and phosphorus content. From Steudel's experiments, it may be concluded that a sufficient standard for the purity of a yeast nucleic acid prepared by alkali extraction is a negative biuret test and a theoretical content of guanine. As both of these requirements are easily determined, it becomes a simple matter to decide whether a given nucleic acid is pure.

The method which we used in preparing yeast nucleic acid is closely analogous to Steudel's procedure, although it is not an exact duplicate of his method. After many unsuccessful attempts to prepare a protein-free nucleic acid, the following procedure was adopted and was found to give a biuret-free product in every case.

Three hundred grams of starch-free yeast, containing about 70% of moisture, was suspended in water and cooled to 0° in the ice box. To this cooled suspension was added 322 cc. of sodium hydroxide solution which contained 0.31 g. of sodium hydroxide per cubic centimeter and which also had been cooled to 0°. The suspension was then diluted to a volume of 2 liters. The temperature was kept at 0° for two hours. Acetic acid was then added until the solution was just acid to litmus. (The PH of the solution was about 6.5.) When the solution had been neutralized its temperature was 15°. The suspension was centrifuged and a slightly turbid liquid resulted. To this was added enough alcohol to produce a solution containing 4% of alcohol. When this solution was filtered a sparkling clear filtrate was obtained. Enough concentrated hydrochloric acid was added to make the filtrate just acid to congo red paper, and finally an equal volume of 95% alcohol. A colorless, flocculent precipitate formed immediately. This was centrifuged, washed twice with 95% alcohol, then with ether three times. The product thus obtained was entirely biuret free, was perfectly white and contained the theoretical quantity of guanine as determined by the method described by Jones in his monograph on nucleic acids.[10] Several preparations of nucleic acid were made in this manner and a protein-free product was obtained in every case. The weight of the air-dried nucleic acid from 300 g. of moist yeast was usually between 4 and 5 g.

---

[6] Altmann, *Arch. Anat. Physiol.*, 1889, 526.

[7] Baumann, *J. Biol. Chem.*, 33, Proceedings *XIV* (1917–1918).

[8] Levene and La Forge, *Ber.*, 43, 3165 (1910).

[9] Steudel, *Z. physiol. Chem.*, 131, 159 (1923).

[10] Walter Jones, "Nucleic Acids," Monograph on Biochemistry, Longmans, Green and Co., New York City, 1920, p. 107.

The Separation of Cytosine from Thymine.—If the acetol test for 5-methylcytosine is to be applied to the cytosine fraction of any nucleic acid molecule, it becomes absolutely necessary to know whether cytosine can be separated from thymine and the acetol test made negative on the cytosine so obtained. In case this specific test cannot be made negative in the cytosine unit when this pyrimidine is separated from mixtures known to contain only cytosine and thymine, it is obvious that the acetol test would be of no value in ascertaining the presence of 5-methylcytosine in the basic aminopyrimidine fraction of a nucleic acid, which is known to contain thymine. The following experiment was, therefore, carried out.

To 0.5 g. of pure cytosine and 2.0 g. of thymine (both of synthetic origin) dissolved in one liter of water, enough concentrated sulfuric acid was added to make the solution 5% in strength (50 g.). A 10% solution of phosphotungstic acid was then added until a precipitate ceased to form. This precipitate was removed by means of the centrifuge and decomposed in the usual manner by trituration with barium hydroxide solution. The barium phosphotungstate was separated by centrifugation and the excess of barium then removed by precipitation with carbon dioxide. The clear and practically colorless solution was diluted to a volume of one liter, the acidity adjusted to 5.0% and the phosphotungstic acid precipitation repeated and carried out as in the first case. The neutral solution containing the cytosine was evaporated to a volume of 50 cc. and tested for thymine in the usual way. A negative result was obtained. In other words, the aminopyrimidine cytosine can be freed from all traces of thymine by means of phosphotungstic acid. Since it is known that 5-methylcytosine and cytosine behave in a similar manner when treated with phosphotungstic acid, it can be concluded from the result of this experiment that it will be possible to apply the acetol test for determination of the presence of 5-methylcytosinc in any nucleic acid after preliminary hydrolysis of the nucleic acid molecule.

The Hydrolysis of Yeast Nucleic Acid.—Part of the nucleic acid used in this research was a special product obtained from the firm of Merck and Company. It was found to be protein-free and to contain the theoretical quantity of guanine. The pyrimidine fraction was isolated according to the following procedure.

To 50 g. of nucleic acid was added 300 cc. of water and 100 cc. of concentrated sulfuric acid. The mixture was heated in an oil-bath at 125° for twenty-five hours. The operation was conducted in a one-liter round-bottomed flask connected to a reflux condenser. At the end of this time the mixture was cooled and to it was added 3.6 liters of water. Finely-powdered barium hydroxide was then added until the solution was distinctly alkaline to litmus. The barium sulfate was centrifuged out, the precipitate suspended in two liters of hot water and again centrifuged. The two solutions were combined and concentrated *in vacuo* to a volume of 2 liters. Sulfuric acid was added to this solution until it was distinctly acid, the solution heated to its boiling point and filtered. To the filtrate was added a hot aqueous solution of silver sulfate (36 g.). A voluminous chocolate-colored precipitate came down immediately (the silver salts of the purines). This was filtered off and the solution made alkaline with barium hydroxide to precipitate the silver salts of the pyrimidines. Addition of barium hydroxide was continued until a precipitate no longer formed. The solution was thoroughly cooled and the silver salts of the pyrimidines were centrifuged out. After washing the precipitate with water, it was suspended in 2 liters of water, stirred thoroughly to break up any lumps, heated to 60°, made acid with 30 cc. of concentrated sulfuric acid and hydrogen sulfide passed into the solution for several hours. The silver sulfide was filtered off, suspended in hot acid solution and hydrogen sulfide passed in for another two hours to insure complete decomposition of silver salts. The silver sulfide was then removed by means of the centrifuge and the liquid added to the solution obtained from the first centrifugation. The sulfuric acid was removed from this solution with barium hydroxide and the excess of barium removed with carbon dioxide. The clear solution so obtained was concentrated in *vacuo* to a volume of 100 cc. Fifty cc. of this solution was treated with bromine and then made alkaline with barium hydroxide. The purple barium salt of dialuric acid was filtered off and to the filtrate was added 2 g of barium hydroxide crystals. This mixture was heated under a reflux condenser for fifteen minutes and then distilled to remove acetol. When the distillate so obtained was tested for acetol, a faint but distinct fluorescence could be observed. This would seem to indicate the presence of a small amount of either thymine or 5-methylcytosine. This assumption was not true. The fluorescence was found to be due to acetol arising from a small quantity of nucleosides contained in the pyrimidine fraction. Baudisch has shown that all the simpler carbohydrates, including pentoses, give rise to acetol when distilled with alkali.[11] Hence, an acetol test is not conclusive evidence as to whether either thymine or 5-methylcytosine is present in the pyrimidine fraction until it has been shown that distillation with alkali alone gives a negative acetol reaction.

The following experiment, therefore, was carried out to prove that the acetol test did not come from either thymine or 5-methylcytosine: 50 g. of nucleic acid was hydrolyzed for twenty-five hours with 33% sulfuric acid as described above. The solution containing the pyrimidine was concentrated to a volume of 100 cc., 33 cc. of concentrated sulfuric acid added and the mixture refluxed for twelve hours at 135". The mixture was then cooled and diluted with 2 liters of water and the sulfuric acid and barium removed in the usual way. The neutral solution was concentrated over a free flame to a volume of 100 cc. To 20 cc. of this solution was added 2 g. of barium hydroxide and the mixture refluxed for fifteen minutes. The distillate from this mixture gave a negative test for acetol, no fluorescence being observed even with the mercury arc light. It may be concluded from this experiment that the pyrimidine fraction tested was completely free of nucleosides. A second experiment was carried out with 20 cc. of the mixture. Bromine was added in excess, the excess removed by boiling and the solution made alkaline with barium hydroxide. The purple precipitate was removed by filtration. Two grams of barium hydroxide was added to the filtrate and the mixture refluxed for fifteen minutes as in the preceding experiment. The distillate from this mixture also gave a negative acetol test. It may be concluded, therefore, that the pyrimidine fraction of yeast nucleic acid, if it contains either thymine or 5-methylcytosine at all, contains these two pyrimidines in a quantity less than 1 mg. per 10 g. of nucleic acid.

Summary

1. A method for preparing a protein-free nucleic acid from yeast has been described. This is based on the original method of Altmann modified as recommended by Steudel.

2. The acetol test for thymine and 5-methylcytosine has been applied to the pyrimidine fraction of yeast nucleic acid, and has been found to be

---

[11] Deuel and Baudisch, THIS JOURNAL, 44, 1581 (1924); Baudisch and Deuel, *ibid.*, 44, 1585 (1924); Baudisch, *Biochem.* Z., 89, 279 (1918).

negative. It may be concluded, therefore, that neither of these pyrimidines is present in yeast nucleic acid.

3. By application of the acetol test for 5-methylcytosine to the aminopyrimidine fraction of any nucleic acid, it is now possible to detect this substance when present in very minute quantities.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLVIII. SYNTHESIS OF POLYPEPTIDE-HYDANTOINS FROM HYDANTOIN-1-ACETIC ACID[1]

BY ALICE G. RENFREW[2] AND TREAT B. JOHNSON

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

It is a growing belief that heterocyclic combinations containing active methylene groups (—CH_2—) occur in the structure of normal proteins; therefore, any information which increases the present knowledge of the chemistry of such cyclic groupings is of immediate value in the present period of intense interest in protein chemistry. Any consideration of cyclic amide groupings brings up at once the importance of the ureide structure, and the possible presence of polypeptide-hydantoin combinations in protein molecules. As a result of our chemical study of special bacteria like tubercle bacilli, we have learned that organic combinations are present in these unicellular organisms, some of which may function as inhibitors and some as accelerators of cell growth and development. These facts are important and lead one to ask whether there may not be some truth in the recent query of Prentiss,[3] who writes as follows: "Do chemicals exist in the tissues that are poisonous to infecting organisms and can such be isolated and made in sufficient quantities so that they could be used not only in the treatment of these infections, but possibly also in prevention in special instances? The presence of such substances is only hypothetical but the same may be said of numerous others commonly referred to in medical work as vitamines and whose presence we do not doubt." In fact, H. Kossel[4] studied the action of nucleic acid, a common constituent of cellular tissue, on bacteria and actually found that cholera germs and streptococci are readily killed

---

[1] This investigation was supported in part by a grant from the Therapeutic Research Committee of the Council on Chemistry and Pharmacy of the American Medical Association.

[2] Constructed from a dissertation presented by Alice Gertrude Renfrew to the Faculty of the Graduate School of Yale University, in June, 1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Prentiss, "The Specific Immunity of the Tissues and Its Bearing on Treatment," *Science*, 62, 91 (1925).

[4] Kossel, Nature, 49, 240 (1894).

by small quantities of the acid. Anthrax germs were more resistant. He considers that the bactericidal action of lymph cells is due in part at least to the action of nucleic acids. Thus in the consideration of medicinals there may be particular value in the study of structures resembling those functioning in characteristic biochemical products, and it is for such reasons that we emphasize the importance of both acyclic and cyclic peptide linkages.

In our last paper on the chemistry of hydantoins[5] we recorded the behavior toward aldehydes of 2-thiohydantoin-3-acetic acid and its oxygen analog and showed that only one methylene grcup in this combination is characterized by its pronounced reactivity toward aldehydes. In no case thus far studied have we observed an aldehyde condensation involving the methylene group of the substituent acetic acid radical. In other words, the methylene group $—CH_2—$ is activated by linkage in cyclic combinations as represented by hydantoin and diacipiperazine cycles. Whether corresponding side-chain substitutions in diacipiperazines will interact with aldehydes remains to be determined.

Instances of condensations in which an N-1-substituted hydantoin has been used with an aliphatic group joined to nitrogen adjacent to the methylene carbon are fairly numerous but scattered. In working with such substitution products very inconsistent results have been obtained and the reactivity of the cyclic methylene groups in these combinations has been a debatable question. Since both groupings $—NHCH_2CO—$ and $=NCH_2CO—$ may actually function in amino acids and polypeptides, there is, therefore, a general interest in any reaction that may contribute to a better understanding of the properties inherent in these structures.

According to our present knowledge we are justified in claiming that the methylene group of the hydantoin or thiohydantoin ring is more reactive toward aldehydes than is the methylene radical in acyclic combinations like hippuric acid. This reactivity is decidedly influenced, however, by substitution of aliphatic groups on nitrogen of the hydantoin cycle. Biltz[6] reported practically complete recovery of 1,3-dimethylhydantoin after heating this hydantoin with benzaldehyde in the presence of sodium acetate, acetic acid and acetic anhydride. Working with ethyl hydantoin-1-acetate Johnson and Bates[7] did not succeed in bringing about a condensation with benzaldehyde. No difficulty was encountered in accomplishing condensations by the use of N-1 acyl derivatives like 1-acetylhydantoin[8] and 1-benzoyl-2-thiohydantoin.[9] Erlenmeyer, Jr., also succeeded in condensing creatinine with benzaldehyde in the presence of acetic anhydride, giving

---

[5] Renfrew and Johnson, THIS JOURNAL, **51,** 254 (1929).

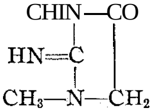
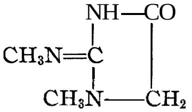
[6] Biltz, Ber., **45,** 1673 (1912).

[7] Johnson and Bates, THIS JOURNAL, 38, 1087 (1916).

[8] Johnson and Wrenshall, *ibid.,* **37,** 2133 (1915).

[9] Johnson and Kohmann, *ibid.,* **37,** 1863 (1915).

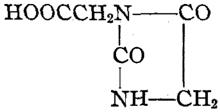
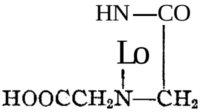
benzalacetylcreatinine.[10] By simple changes in experimental conditions Nicolet and Campbell[11] obtained better yields than those reported by Erlenmeyer, Jr. That creatinine interacts so favorably with aldehydes in acetic anhydride solution is possibly due to the fact that acetylation occurs before condensation, thereby leading to activation of the cyclic methylene group. With substituted glycocyamidine or methylcreatinine like I and II,[12] all attempts by Nicolet and Campbell to bring about condensation

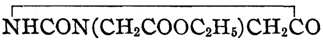
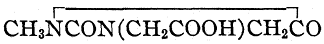
I  or  II

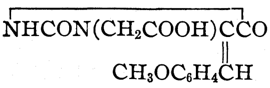
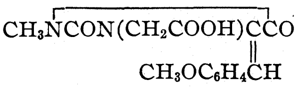
were unsuccessful. Consequently they were unable to obtain any direct evidence as to the structure of the methylation products of creatinine by this method of attack. With 1-methylhydantoin they did succeed in effecting a condensation with benzaldehyde, but only with a yield of 32% of the theoretical. In all the work of Nicolet and Campbell no record is made of the identification of any geometric isomers.

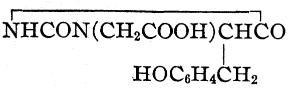
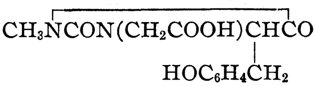
Since the ultimate object of the present research was to develop methods for preparing specific compounds which might exhibit favorable properties as antiseptics, it was important that both N-1 and N-3 acetic acid derivatives of phenolic hydantoins be studied. As stated in our previous paper[6] the introduction of the acetic acid group was expected to increase solubility and lower toxicity of such combinations.

The reactivity of hydantoin-1-acetic acid, IV, toward an aldehyde has now been investigated by us, and a description of the different condensation products resulting from the action of anisaldehyde is given in the Experimental Part of this paper. The reactions that we desire to report at this time are recorded below.

III  IV 

V  VI 

VII  VIII 

IX  X 

---

[10] Erlenmeyer, Jr., and Früstück, *Ann.*, **284**, **36** (1895).

[11] Nicolet and Campbell, THIS JOURNAL, 50, 1155 (1928).

[12] Korndorfer, *Arch. Pharm.*, **242**, 641 (1900); Kunze, *ibid.*, **248**, 578 (1910).

In our research the acid, IV, was used in the form of its ethyl ester, V.[13] When this is condensed with anisaldehyde in the presence of sodium acetate and in acetic acid, the product of reaction is the sodium salt of anisalhydantoin-1-acetic acid, VII. The yield, however, is only 34% of the theoretical and thus far no geometric isomer has been identified. Alkylation of the hydantoin (V) with methyl iodide gives the methylhydantoin represented by Formula VI. When the latter is condensed with anisaldehyde under the usual conditions, two products of reaction result in small yields,[14] namely, the sodium salts of the two geometric isomers of 3-methylanisalhydantoin-1-acetic acid melting at 203–205° and 168–169°, respectively.[15] The results obtained by alkylation with methyl iodide were of special value as they enabled us to decide conclusively that the methylene radical in the N-1-acetic acid group is not the reactive position in ethyl hydantoin-1-acetate, V. Alkylation of anisalhydantoin-1-acetic acid, VII, gave the hydantoin, VIII, which underwent reduction with hydriodic acid, forming 3-methyl-5-hydroxybenzylhydantoin-1-aceticacid, X.[15] This same hydantoin, X, is also formed by the action of hydriodic acid on the two geometric isomers represented by Formula VIII and resulting by condensation of anisaldehyde with the hydantoin, VI. In other words, the reactive methylene group —CH_2— in both N-1- and N-3-hydantoin-acetic acids is the one in cyclic combination. In neither case did we observe any evidence of any other type of condensation reaction.

Experimental Part

Ethyl Hydantoin-1-acetate, V.—The imino-acetonitrile from which this compound was synthesized was prepared according to the method used by Bailey and Snyder[16] and later applied successfully by Johnson and Rinehart.[17] Bailey and Snyder report a 44% yield of the hydantoin ester. In several repetitions of this preparation we have consistently obtained yields varying from 35 to 45%. The ester melts at 85°.

5-p-Anisalhydantoin-1-acetic Acid, VII.—The reagents utilized for the preparation of this compound were applied in the following proportions: ethyl hydantoin-1-acetate, 7 g.; anisaldehyde, 6.3 g.; anhydrous sodium acetate, 8 g.; glacial acetic acid, 12 cc., and acetic anhydride, 3 cc. After refluxing this mixture for six hours the resulting solution was diluted with water and the reaction product separated by filtration. This was identified as the sodium salt of anisalhydantoin-1-acetic acid. It was colorless and had no definite melting point, charring badly when heated above 300". The yield of this salt was about 34% of the theoretical. Apparently all of the hydantoin-1-acetate that reacted with aldehyde underwent saponification in the proccss, as we obtained no

---

[13] Bailey and Snyder, THIS JOURNAL, 37, 940 (1915); Jongkess, *Rec. trav. chim.*, **27**, 287 (1908).

[14] It may be predicted from our past experience that the sulfur analog, ethyl 3-methylhydantoin-1-acetate [Bailey and Snyder, THIS JOURNAL, **37**, 940 (1915)], will be found to condense more easily with anisaldehyde.

[15] Hahn and Renfrew, *ibid.*, **47**, 147 (1925).

[16] Bailey and Snyder, *ibid.*, 37, 935 (1915).

[17] Johnson and Rinehart, *ibid.*, 46, 768 (1924).

evidence of the formation of ethyl anisalhydantoin-acetate. Allowing for the fact that 55% of anisaldehyde was recovered, the yield of condensation product was 54% of the theoretical.

When this salt was dissolved in water and the solution was acidified with hydrochloric acid, the hydantoin-1-acetic acid separated. This acid is difficultly soluble in alcohol and water and moderately soluble in glacial acetic acid. It melts at 215–216° (uncorr.). The acid crystallizes from ethyl alcohol with one molecule of alcohol of crystallization which it loses at 110°.

Anal. Calcd. for $C_{13}H_{12}O_5N_2 \cdot C_2H_5OH$: N, 8.70. Found: N, 8.88, 9.00.

Anal. (after drying at 110°). Calcd. for $C_{13}H_{12}O_5N_2$: N, 10.14. Found: N, 9.85, 9.90.

In order to increase the yield of this condensation product, we incorporated other condensing agents besides sodium acetate as acetic anhydride and piperidine. With acetic anhydride the unchanged ethyl hydantoin-1-acetate was nearly all recovered after digesting with anisaldehyde for four hours. The ethyl hydantoin-1-acetate was also recovered unaltered when piperidine was employed as a condensing agent.

5-p-Hydroxybenzylhydantoin-1-acetic Acid, **IX.**—This hydantoin was formed when the preceding unsaturated hydantoin was reduced with hydriodic acid. The following proportions were used in the reaction: anisalhydantoin-1-acetic acid, 1.3 g.; hydriodic acid (sp. gr. 1.7) 6.5 cc., and red phosphorus, 0.4 g. The reduction was carried out at 105° for three hours, when methyl iodide was evolved in quantitative yield. After diluting with about 20 cc. of water and filtering from phosphorus, the excess of hydriodic acid was expelled by evaporation; the reduced hydantoin finally separated in a crystalline condition. The hydantoin was purified by crystallization from water and melted at 201°.

Anal. Calcd. for $C_{12}H_{12}O_5N_2$: N, 10.60. Found: N, 10.54, 10.50.

3-Methyl-5-p-hydroxybenzylhydantoin-1-acetic Acid, X.—The structure of 5-*p*-hydroxybenzylhydantoin-1-acetic acid and the corresponding anisal precursor was established conclusively as follows. The anisalhydantoin-1-acetic acid was first methylated by the action of methyl iodide in methyl alcohol in the presence of the required proportion of potassium hydroxide. The products of reaction were the methyl ester of 3-methylanisalhydantoin-acetate and the corresponding methylhydantoin-acetic acid. Both of the compounds were reduced by hydriodic acid and red phosphorus to the above methylated hydantoin, 3-methyl-5-p-hydroxybenzyl-hydantoin-1-acetic acid. This hydantoin proved to be identical with the methyl-p-hydroxybenzylhydantoin-1-acetic acid previously described by Hahn and Renfrew,[15] and there was no lowering of the melting point when a mixture of the two was heated in a capillary tube (167°). The formation of this methylated compound proves conclusively that ethyl hydantoin-1-acetate does not condense with anisaldehyde to form a hydantoin having the constitution XI represented below.

$$\text{XI}\quad CH_3OC_6H_4CH=C(COOH)\text{—}\overline{NCH_2CONHCO}$$

In other words, the methylene group in the hydantoin cycle is the reactive complex when brought into reaction with aldehydes.

Ethyl 3-Methyl-hydantoin-1-acetate, $CH_3\overline{NCON(CH_2COOC_2H_5)CH_2CO}$.—Three grams of ethyl hydantoin-1-acetate dissolved in 15 cc. of methyl alcohol was combined with a solution containing 2.4 equivalents of sodium methylate. This solution, from which an organic salt crystallized as it formed, was refluxed for eight hours and then digested with an excess of methyl iodide. When the reaction was complete, as indicated by the neutrality of the solution, sodium chloride was separated by filtration and the solution concentrated under diminished pressure. On diluting the concentrated alcohol solution with water and again evaporating to remove alcohol, the ethyl 3-methyl-hydantoin-1-acetate was finally separated by extraction with chloroform. After removing the chloroform the ester was finally purified by crystallization from alcohol. It separated in small, glistening plates melting at 91–92°. The sulfur analog of this ester **has** been described by Bailey and Snyder.[16]

Anal. Calcd. for $C_8H_{12}O_4N_2$: N, 14.0. Found: N, 14.11, 13.96.

3-Methyl-5-p-anisalhydantoin-1-acetic Acid, VIII.—This compound was prepared by condensing 3-methylhydantoin-1-acetic acid with *p*-anisaldehyde in the presence of sodium acetate in glacial acetic acid solution Here again the product of reaction was a sodium salt which gave the above acid when treated with hydrochloric acid. The high-melting modification of this acid was the first product obtained (melting point 203–205°).[15]

When the crude condensation mixture was extracted with ether in a Soxhlet and the solvent concentrated, a solid residue containing sodium remained behind. This was dissolved in water and on the addition of hydrochloric acid to this salt solution an immediate precipitate was produced. On recrystallization from dilute alcohol it melted at 168–169° and was identified as the labile modification of 3-methyl-5-p-anisalhydantoin-1-acetic acid.[15] The yield of either isomer was small.

Interesting results were obtained when the picric acid reaction[18] for a carbonyl group was tried on the above hydantoins. Ethyl hydantoin-1-acetate failed to give the red-brown color characteristic of hydantoin-3-acetic acid, but did give an intense orange-red coloration. On the other hand, both hydroxybenzylhydantoin-1-acetic acid and 3-methyl-p-hydroxybenzylhydantoin-1-acetic acid gave negative reactions.

Summary

1. Hydantoin-1-acetic acid condenses with aldehydes with formation of substituted derivatives. These condensations involve a reaction of the cyclic methylene group —CH_2— of the hydantoin cycle.
2. Hydantoin-1-acetic acid is less reactive than its isomer, hydantoin-3-acetic acid.
3. Thus far no evidence has been obtained of the formation of geometric isomers.
4. The biological importance of hydantoin-acetic acids is emphasized, and also their possible structural relationship to proteins.

NEW HAVEN, CONNECTICUT

---

[18] Brand and Sandburg, J. *Biol. Chem.*, 70, 381 (1926).

[CONTRIBUTION NO. 38 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE DEARRANGEMENT OF NITROUREA AND ITS APPLICATION IN SYNTHESIS

BY TENNEY L. DAVIS AND KENNETH C. BLANCHARD

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

Nitrourea might be expected to dearrange[1] in two modes to form on the one hand (1) nitroamide and cyanic acid, and on the other (2) ammonia and nitrocyanic acid. The nitro group would promote the dearrangement and the molecule would fall apart more readily than does the molecule of urea. We have found abundant proof of dearrangement of the first sort," but only meager evidence for that of the second. We have isolated nitroamide and cyanic acid from solutions of nitrourea and have prepared nitrourea by the combination of nitroamide with cyanic acid. Since nitrourea dissolved in water dearranges in part into nitroamide and cyanic acid, and since nitroamide decomposes into nitrous oxide and water, it follows that an aqueous solution of one equivalent of nitrourea may be used, with great advantage, for purposes of synthesis as if it were a solution of one equivalent of cyanic acid itself.

Nitrourea decomposes on melting with the evolution of gas and yields a sublimate and a solid residue. The gases consist of water, nitrous oxide, cyanic acid, carbon dioxide and ammonia, and the solid materials of monoammonium cyanurate along with small quantities of ammelide, urea and biuret. These are the products which would be expected from the predicted dearrangements. The nitroamide breaks down into water and nitrous oxide. The cyanic acid in part escapes as such, in part combines with ammonia to form urea and in part polymerizes to form cyanuric acid, which combines with a portion of the ammonia to form ammonium cyanurate—and the latter substance by loss of water yields ammelide. Although nitrocyanic acid, $O_2N\text{-}NCO$, is not a known substance, it would, from analogy with known nitramines, be expected to decompose into nitrous oxide and carbon dioxide. The presence of ammonia and of carbon dioxide in the products of the decomposition of nitrourea by heat suggests strongly that this substance does dearrange into nitrocyanic acid and ammonia, but constitutes the only real evidence which we have found on that point. The presence of biuret might perhaps be explained by supposing that it is formed, as Werner[2] supposes it to be formed in aqueous solution, by the combination of cyanic acid with urea. We have found that

---

[1] *Cf.* (a) Davis and Underwood, THIS JOURNAL, 44, 2595 (1922); (b) Davis and Blanchard, *ibid.*, 45, 1816 (1923); (c) Davis, *Proc. Nat Acad Sci.*, **11**, 68 (1925); (d) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, *61*, 437 (1926); *(e)* Davis and Luce, THIS JOURNAL, 49,2303 (1927).

[2] Werner, "The Chemistry of Urea," Longmans, Green and Co., London, 1923, p. 25.

urea and cyanic acid do not combine in aqueous solution to form biuret, and prefer the more likely explanation that the cyanic acid combines with itself to form a dimer, dicyanic acid, NH_2–CO–NCO, which then combines with ammonia to form biuret—but wish to reserve a fuller discussion of the matter for a later paper.

When nitrourea is boiled with water, the nitroamide which results from its dearrangement breaks down completely, and nitrous oxide is given off quantitatively. Experiments in which nitrourea was heated with water in a sealed tube until gas was no longer produced, and in which silver nitrate was then introduced into the solution without opening the tube, showed that the production of cyanic acid is also quantitative.

A freshly prepared aqueous solution of nitrourea does not give the biuret test. After boiling it gives the biuret test, but contains no biuret. On evaporation to dryness, it yields a residue of practically pure urea, evidently formed by the combination of cyanic acid with ammonia produced by the hydrolysis of another portion of the cyanic acid.

The great ease with which nitrourea dearranges in aqueous solution may be shown by several striking experiments. A freshly prepared cold aqueous solution of nitrourea gives with silver nitrate a white crystalline precipitate of silver nitrourea. When the liquid is warmed, the precipitate dissolves; when this clear liquid is boiled for a minute or two, it deposits an insoluble precipitate of silver cyanate. If the freshly prepared solution is boiled, cyanic acid may be detected by its vinegar-like odor in the gases which are evolved. A freshly prepared cold solution gives, with copper sulfate and pyridine, a lilac-colored crystalline precipitate of copper pyridine nitrourea, insoluble in chloroform. The boiled solution with these reagents gives no precipitate, but the liquid yields a blue chloroform extract which contains copper pyridine cyanate. When copper pyridine nitrourea is allowed to stand in contact with water and chloroform at laboratory temperature, the chloroform turns blue after only a few hours, and if the mixture is allowed to stand overnight the copper pyridine nitrourea disappears entirely. Nitrourea recrystallized from warm, not boiling, water, under conditions where no gas is evolved, has an indefinite melting point between 135 and 150°. It may be obtained perfectly pure by recrystallization from ether, benzene or chloroform, in which solvents it does not dearrange, and melts sharply at 158.4–158.8° with decomposition.

We have obtained nitroamide from the dearrangement of nitrourea by dissolving the latter substance in water, warming until active gassing had commenced, freezing in liquid air, drying out the ice by triturating it with anhydrous sodium sulfate, extracting with ether, and finally by concentrating the ether extract and precipitating with petroleum ether. The resulting nitroamide, identified by its properties and by analysis, was found on heating to break down quantitatively into water and nitrous oxide.

We have also isolated nitroamide from a solution of urea nitrate in concd. sulfuric acid. We have shown that the dearrangement is reversible by producing nitrourea by the direct combination of nitroamide and cyanic acid, by stirring together silver cyanate and an aqueous solution of nitroamide to which dilute hydrochloric acid had been added.

Nitrourea dissolves in cold concd. sulfuric acid to form a solution which contains cyanic acid and nitroamide. On standing the sulfuric acid dehydrates the nitroamide slowly, nitrous oxide comes off, the mixture warms up, the cyanic acid is hydrated in part to form carbon dioxide and the effervescence becomes vigorous. Such a solution after effervescing actively for about an hour exploded with a distinctly audible puff and visible flash but without any damage to the beaker in which it was contained. The nitroamide which is present in a cold solution of nitrourea in concd. sulfuric acid may also combine with water under the hydrating action of the sulfuric acid to form nitric acid, and does this if the environment is such that the nitric acid may enter into other reactions. Such a solution in the nitrometer gives up quantitatively the nitrogen corresponding to the nitro group of its nitrourea.[3] We have used such a solution for the nitration of aniline, phenol, acet-*p*-toluide and cinnamic acid, in a manner similar to that in which a sulfuric acid solution of nitroguanidine has been used.[1d] No gas is given off if the nitration mixtures are kept below 0°. If they are allowed to warm up, effervescence becomes violent.

The spontaneous decomposition of nitrourea in aqueous solution is influenced by acids and by bases in the same way as the spontaneous decomposition of nitroamide.[4] The substance may be recrystallized without change from boiling water or from boiling alcohol if the solvent contains a small amount of sulfuric acid. Inorganic and organic bases promote the decomposition. We have noted in a number of cases that pure air-dried nitrourea stored in soft glass bottles decomposes after a few months, blowing out the stopper, giving off ammonia and leaving a pasty residue which contains water, urea and ammonium cyanurate, and have been able to show that the effect is due to the alkali of the glass which is dissolved by the water retained in the air-dried nitrourea. The decomposition does not occur in hard glass even if moisture is present, but does occur in hard glass if the sample is moistened with an aqueous extract of soft glass. It does not occur in an atmosphere dried with phosphorus pentoxide, even when sodium bicarbonate is in contact with the nitrourea.

Strong ammonia water dropped upon nitrourea hisses like water on phosphorus pentoxide. When an excess is used and the solution is evaporated to dryness, pure urea is obtained quantitatively. When one molecular equivalent of aniline is dissolved in a saturated aqueous solution of

---

Tope and Barab, THIS JOURNAL, 38,2552 (1916).

[4] Brönsted and Pedersen, *Z. physik.* Chem., 108, 189 (1924).

nitrourea and the liquid is allowed to stand at laboratory temperature, crystals of phenylurea are found to have separated after twenty-four hours, and after forty-eight hours the yield is nearly quantitative. When nitrourea is added to an aqueous solution of a primary aliphatic amine, such as methylamine, the reaction is very vigorous and requires cooling to moderate it. With less basic amines the reaction is correspondingly slower. Since the mono-substituted aliphatic ureas dearrange but little in boiling water, the reaction mixtures may be evaporated hot and give excellent yields of pure products. With suitable variations of procedure, we have prepared, from the corresponding primary amines, methylurea, ethylurea, n-butylurea, benzene-azo-phenylurea, ethylene-diurea, *m*- and *p*-uraminobenzoic acid, sodium *p*-uraminobenzene-sulfonate, hydantoic acid, a-uramino-a-isobutylacetic acid and ethyl hydantoate. The advantages of the method are especially apparent in the cases of methyl- and ethylurea. Nitrourea yields nothing but gases and a principal product which is practically pure at once and not deliquescent, while the older method with potassium cyanate and the hydrochloride of the amine yields a product which is contaminated with mineral salts and is deliquescent and difficult to purify.

By the same general method we have prepared, from nitrourea and the corresponding secondary amines, α,α-dimethylurea, α,α-diethylurea, α,α-di-n-propylurea and its picrate, α,α-di-*n*-butylurea (new) and its picrate (new), α,α-di-*iso*-amylurea and its oxalate and picrate (new), and 2,3,4-trihydroquinolylurea.

Derivatives of urea in which one aromatic and one aliphatic group are attached to the same nitrogen atom dearrange so readily in water solution that any attempt to purify them by recrystallization from that solvent only results in making them less pure. If they are boiled in water solution, they dearrange in part, the cyanic acid is hydrolyzed to ammonium carbonate, the secondary amine escapes with the steam and part of the material is lost. By allowing the amine to stand at laboratory temperature in contact with water and a slight excess of nitrourea until crystals had separated and could be removed, or until the mixture had spontaneously evaporated to dryness, in which case the whole residue was worked up with a non-dearranging solvent like benzene or petroleum ***ether,*** we have obtained α-methyl-α-phenylurea, a-ethyl-a-phenylurea, α-*n*-propyl-α-phenylurea (new), its picrate (new) and oxalate (new), and α-*n*-butyl-α-phenylurea (new) in excellent yields.

In the experiments with di-n-propylamine and n-propylaniline, in addition to the expected urea derivatives, there were obtained, respectively, ω,ω-di-*n*-propylbiuret (new) and ω-*n*-propyl-ω-phenylbiuret (new). No ω,ω-disubstituted biurets have heretofore been described. We have identified our substances by analysis and by comparison with the materials produced by a new method which has been found to be a general one for the preparation of ω,ω-disubstituted biurets, namely, the interaction of nitrobiuret with secondary amines, as described in the next paper of this series. In the present cases the cyanic acid from the dearrangément of nitrourea evidently combines with itself to form dicyanic acid, which then combines with the secondary amine to form the ω,ω-disubstituted biuret.

Nitrourea is but little affected by refluxing with dry alcohols and may be recovered unchanged. When refluxed with moist alcohols, it dearranges; the cyanic acid in part combines with the alcohol to form carbamic ester and in part apparently combines with itself to form dicyanic acid, which then combines with the alcohol to form allophanic ester. We reserve a fuller discussion of dicyanic acid for another paper. Allophanic esters are converted to carbamic esters by refluxing with alcohols. Nitrourea dearranges much more rapidly than urea, and in practice yields more allophanic ester because the solution is not subjected to so long a refluxing. Otherwise the reaction of nitrourea with alcohols has no more interest for purposes of synthesis than the reaction of urea itself.

Experiments

Experiments which are indicated in the foregoing with sufficient clearness are not again discussed in this section.

Preparation of **Nitrourea.**—Nitrourea was prepared by a modification of the original method of Thiele and Lachman.[5] Two hundred grams of carefully dried urea nitrate was added in small portions at a time with stirring to 300 cc. of concd. sulfuric acid[6] (1.84) while the temperature of the mixture was kept below 0°. After the last portion had been added, the cold milky mixture was allowed to stand for one minute and was then poured into a liter of ice and water. The finely-divided white precipitate was collected on the filter, sucked as dry as might be, and, without washing, was immediately dissolved while still wet in boiling alcohol.[7] The liquid deposited pearly leaflets on cooling. It was chilled in ice water before filtering and the crystals were rinsed with cold alcohol. The alcoholic mother liquors were used for the crystallization of several successive hatches. The air-dried product was sufficiently pure without another crystallization. Samples of it have remained unchanged in hard glass bottles for several years; yield, 90% or better.

Decomposition by Heat.—Nitrourea (0.6148 g.) was decomposed by heating at 170° in the vacuum of a mercury pump. The gases were allowed to stand overnight in order that the cyanic acid might polymerize on the walls of the apparatus. There resulted 0.2520 g. of residue (41%) which gave tests for biuret and cyanuric acid but which gave no color with the diphenylamine reagent, and 55.4 cc. of gas (at 761 mm. and

---

[5] Thiele and Lachman, *Ann.*, 288,281 (1895).

[6] Instead of 700 cc. as recommended by Thiele and Lachmann and by Ingersoll and Armendt, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 85.

[7] The precipitate still contained enough acid to prevent the dearrangement of the nitrourea in boiling alcohol. For a second recrystallization it was found to be unsafe to heat the alcohol above 60°.

26°) which consisted of 9.8 cc. (17.8%) of CO_2 and HNCO (absorbed by caustic), 20.96 cc (37.8%) of NH_3 and 24.29 cc. (43.9%) of N_2O.

Twenty-one grams of nitrourea was heated at atmospheric pressure at 158–160° until decomposition commenced. After two or three minutes, when the reaction had subsided, the pasty sublimate was scraped from the condenser and added to the residue from the decomposition, total weight, 12.5 g. (59.9%). The material was entirely soluble in boiling water except for a few milligrams of amorphous matter which was identified as ammelide. The solution on evaporation gave off ammonia and yielded 4.95 g. of mono-ammonium cyanurate, identified hy the fact that it gave off ammonia on warming with sodium hydroxide solution, by the properties of the cyanuric acid obtained from it and by analysis.

Anal. Calcd. for $C_3H_6O_3N_4$: C, 24.66, H, 4.11; N, 38.36. Found: C, 25.4, 25.5; H, 3.6, 3.5; N, 38.3, 38.6.

When dissolved in boiling water, acidified, chilled and filtered, 1.135 g. yielded 0.9943 g. of cyanuric acid (99.2% of the calcd. amount). The mother liquors yielded more cyanuric acid on acidification, and, after chilling, filtration and evaporation to dryness, a residue from which butyl alcohol extracted the urea, 0.07 g., identified by mixed melting point and by its xanthydrol derivative. The final residue yielded a small quantity of biuret, identified by mixed melting point and by the biuret test.

Decomposition in Hot Water.—Samples of nitrourea were dissolved in 10 cc. of water and decomposed by warming until active gas evolution had commenced. The gases were allowed to mix at atmospheric pressure with a confined quantity of air whose temperature, volume and pressure could be measured. Analysis showed that the mixture after the experiment contained only nitrous oxide and the gases normally present in atmospheric air. The results, corrected for the vapor pressure of water and calculated to 0° and 760 mm. (but not corrected for the solubility of N_2O in water), were as follows: nitrourea, 0.1177, 0.1860; N_2O found, 24.85, 39.10 cc.; calcd., 25.09, 39.64 cc.

For the determination of the cyanic acid produced by the decomposition of nitrourea, experiments were first tried in which solutions were decomposed in stoppered flasks and then precipitated with silver nitrate, but the results were low, evidently because of the loss of cyanic acid with the gases which escaped when the stopper was removed. Precipitation was therefore accomplished before the gases were allowed to escape. Samples of nitrourea were weighed into Carius tubes, 10 cc. of water was added, then a thin glass ampoule containing 15 cc. of $N/10$ silver nitrate solution and the tubes were sealed. They were then wrapped in wire gauze and warmed in the water-bath until gas production had ceased. After cooling, they were shaken to break the ampoule and the contents were mixed. If the tubes were then opened, the outrushing gas was found to carry away a portion of the liquid. The contents were therefore frozen and loss of solution was avoided when the tubes were opened. The solids were filtered off and washed thoroughly, and unconsumed silver in the filtrate was determined by titration with ammonium thiocyanate: nitrourea, 0.1455, 0.1004; $N/10$ $AgNO_3$ consumed, 13.7, 9.5 cc.; HNCO found, 0.05892, 0.04086; calcd., 0.05954, 0.04108.

Ten grams of nitrourea was dissolved in 100 cc. of water, warmed until gas evolution had ceased and evaporated to dryness. Ammonia was given off. The residue weighed 1.9 g. and consisted of practically pure urea. In another experiment with the same quantities the cyanic acid was removed, after gassing had ceased, by the addition of an excess of silver nitrate solution. The liquid on evaporation to dryness yielded a residue (containing silver nitrate) from which hot butyl alcohol extracted only 0.08 g. of urea.

Effect of Certain Other Solvents.—Half-gram samples of nitrourea were boiled with 50 cc. of benzene, ether and chloroform, respectively, under a condenser the upper end of which was sealed to a gas buret containing mercury. No gas was produced in either experiment. Nitrourea recrystallized once from alcohol melted with decomposition at temperatures between 146 and 153°. Recrystallization from glacial acetic acid raised the melting point to 158.3–158.6°, while one crystallization from benzene, ether or chloroform, in which solvents it is sparingly soluble, yielded material melting at 158.4–158.8°. Several recrystallizations from water at 50° yielded material of great purity, melting at 158.1–158.3°, only slightly lower than crystals from ether.

Nitroamide from **Nitrourea.**—Ten grams of nitrourea was dissolved in 100 cc. of water in a large test-tube and warmed in a water-bath at 75° until gas evolution was active. Five cc. of 6 *N* sulfuric acid was added and the liquid was frozen suddenly by immersion in liquid air. The solid mass was broken up in a mortar and extracted with ether previously cooled to −10°. The ice was then allowed to melt and was triturated with anhydrous sodium sulfate until a dry mass was obtained. This was extracted with ten 50-cc. portions of ether. The ether extracts were evaporated separately in a stream of dry air. The first yielded only a very small amount of nitrourea. The second gave crystals of nitrourea which were removed, and the liquid portion when poured into petroleum ether produced a precipitate of shiny flakes of nitroamide. This was purified by dissolving in ether and precipitating with petroleum ether and finally yielded 0.43 g. of nitroamide, pearly white glistening flakes, melting at 72–73° with decomposition into volatile products. Nitrogen by combustion: found, 45.30; calcd. for NH_2NO_2, 45.16.

Nitroamide from Urea Nitrate.—Two hundred and fifty grams of urea nitrate was added in small portions at a time to 800 cc. of concd. sulfuric acid, as if for the preparation of nitrourea. The solution was removed from the freezing mixture and allowed to stand at room temperature until vigorous gassing had commenced, when it was poured onto 1 kilo of cracked ice and filtered through an asbestos filter (50 g. of nitrourea was obtained). Anhydrous sodium sulfate (about 1500 g.) was added to the filtrate until a thick mush was obtained and this was extracted repeatedly by triturating it with 100-cc. portions of ether. The combined ether extracts, dried with anhydrous sodium sulfate and worked up as described above, yielded 0.21 g. of nitroamide. Two repetitions of the experiment gave, respectively, 0.7 and 0.05 g. of nitroamide. The three yields were combined and, after four treatments with ether and petroleum ether, gave 0.51 g. of nitroamide, m. p. 71.5–75°; nitrogen by combustion: found, 46.49, 46.21; calcd., 45.16.

Nitrourea from **Nitroamide.**—Three grams of silver cyanate was suspended in 20 cc. of ice water, and 1.24 g. of nitroamide (from potassium nitrocarbamate) was added. Five cc. of 6 N hydrochloric acid was added drop by drop while the mixture was stirred with a mechanical stirrer. The stirring was continued for half an hour after the acid had been added. The precipitated silver chloride was removed and the clear liquid was evaporated to dryness at room temperature in a stream of dry air. The residue was extracted with ether and the ether on evaporation yielded 0.13 g. of material melting with decomposition at 146–147° and identified as nitrourea by the facts that it gave a blue color with the diphenylamine reagent and yielded phenylurea when warmed with aniline water. Several experiments in which smaller relative amounts of nitroamide were used were unsuccessful. A similar experiment with nitroamide and silver cyanamide failed to yield any nitroguanidine.

Effect of Impurities on the Stability of **Nitrourea.**—Samples of nitrourea were recrystallized from water (at 50°) which contained in solution ferrous sulfate, ferric nitrate, sulfuric acid, urea, urea nitrate and copper nitrate. The several samples, after drying in the air, were placed in corked test-tubes each in the dark and each in an eastern window. None showed any decomposition after six months.

A sample of nitrourea was recrystallized from water which had been previously refluxed for some time with finely-powdered soft glass. Another sample was washed with sodium bicarbonate solution. One half of each was dried quickly in vacuum over phosphorus pentoxide and put away in sealed glass tubes. The other half of each was dried in the air and placed in corked vials. Of the air-dried samples, that which had been washed with sodium bicarbonate decomposed in two days and that which had been recrystallized from the glass extract in nine days. The pentoxide-dried samples in the sealed tubes showed no signs of decomposition after four months. The tubes were then opened and the contents were emptied onto watch glasses which were allowed to stand in the laboratory under inverted beakers. The sample containing sodium bicarbonate decomposed after three weeks, and that containing glass extract after nine weeks.

Preparation of Mono-substituted Ureas.—The primary amine and slightly more than one molecular equivalent of nitrourea were brought together in water, the mixture was warmed to start the reaction or cooled to moderate it and the product was isolated either by filtration or by evaporating the reaction mixture to dryness. Yields are indicated below.

TABLE I

MONO-SUBSTITUTED UREAS

Product	Yield, %	M. p., °C.	Remarks
Methylurea	85	102	Stout needles from dry acetone
Ethylurea	80	92.1–92.4	Crystals from benzene
n-Butylurea[a]	91	96	Fine needles from benzene
Benzene-azophenylurea[b]	3	222–223	Crystals from alcohol
Ethylene-diurea[c]	78	193–194	Crystals from water; decomposes at 200°
m-Uraminobenzoic acid[d]	90	269.5–270.2	Very fine needles from water
p-Uraminobenzoic acid	Not determined		Microscopic needles from water; does not melt at 275°
Sodium p-uraminobenzenesulfonate[e]	Not determined		
Hydantoic acid[f]	60	160–161	Crystals from 50% alcohol
α-Uramino-α-*iso*butylacetic acid[g]	Not determined		
		186–187	Crystals from 90% alcohol
Ethyl hydantoate	62	134–135	Crystals from 50% alcohol
Phenylurea	98	147	Thick needles from water

[a] Werner, J. Chem. *Soc.*, 115, 1101 (1919), has erroneously reported the melting point as 86°. Butylurea is very readily soluble in water, from which it crystallizes on slow evaporation in thin laminated plates. We have obtained plates 11–12 mm. wide and 50–60 mm. in length.

[b] Benzene-azophenylurea has been prepared by Sonn, *Ber.*, 47, 2443 (1914), by the action of potassium cyanate on amino-azobenzene in acetic acid solution and by boiling an acetic acid solution of amino-azobenzene and urea. The low yield in our experiment is due to the fact that amino-azobenzene is very sparingly soluble in water.

[c] Previously prepared by Volhard, *Ann.*, 119, 394 (1861), by the interaction of silver cyanate with ethylenediamine hydrochloride. He reported it as colorless needles, m. p. 192°.

[d] Previously prepared by Menschutkin, Ann., 153, 84 (1870), by fusing together urea and m-aminobenzoic acid. He reported, m. p. 269–270°.

[e] Sodium *p*-uraminobenzenesulfonate has been prepared by Pellizzari and Matteucci, Ann., 248, 156 (1888), by heating together urea and sodium sulfanilate, and the potassium salt by evaporating to dryness a solution of sulfanilic acid and potassium cyanate. We find that nitrourea warmed with an aqueous solution of sulfanilic acid decomposes and gives off gas, but the cyanic acid so produced does not combine with the sulfanilic acid—and we have recovered the unchanged sulfanilic acid quantitatively. By warming nitrourea with an aqueous solution of sodium sulfanilate, concentrating and pouring into alcohol, we have obtained white crystals of sodium *p*-uraminobenzenesulfonate, identical with those described by Pellizzari and Matteucci.

[f] Lippich, Ber., 41, 2959 (1908), reports a melting point of 153–156° in an open tube and 163° in a closed tube. We find m. p. 160–161° in an open melting-point tube.

[g] Lippich reports, m. p. 188–189° in a closed tube. We find, m. p. 186–187" in an open tube.

We have not been able to secure any urea derivatives from the interaction of nitrourea with *p*-aminoacetophenone and with acetamide.

Preparation of α,α-Dialkylureas.—The preparation of these substances was carried out in essentially the same way as the preparation of the monosubstituted ureas.

TABLE II

α,α-DIALKYLUREAS

Product	Yield, %	M. p., °C.	Remarks
α,α-Dimethylurea	88	182	Crystals from alcohol
α,α-Diethylurea[a]	65	75.0–75.3	Pearly oblong plates from absolute ether
α,α-Di-*n*-propylurea	57	75.8–76.1	Waxy needles from petroleum ether
Picrate[b]	..	136	Recrystallized from water
α,α-Di-*n*-butylurea	86	...	Colorless oil at ordinary temp. Nitrogen: Found, 16.13; calcd. for $C_9H_{20}ON_2$, 16.27
Picrate[e]	..	82–83	Small plates from water–alc. Nitrogen: Found, 17 29; calcd. for $C_{15}H_{23}O_8N_5$, 17 45
α,α-Di-*iso*-amylurea	92	...	Colorless oil at ordinary temp.
Oxalate[d]	..	101.5–102	
Picrate[e]	..	72.8–73.9	Small prisms from water–alc. Nitrogen: found, 16.26; calcd. for $C_{17}H_{27}O_8N_5$, 16.34
2,3,4-Trihydroquinolylurea[f]	85	146.2–146.6	Colorless needles from water

[a] Franchimont, Rec. *trav. chim.*, 2, 122 (1883), reported m. p. 70°, and van der Zande, *ibid.*, 8, 226 (1889), m. p. 74". Ordinary laboratory ether is not a suitable solvent for the recrystallization of α,α-diethylurea.

[b] Melting point in agreement with McKee, Am. Chem. J., 42, 16 (1909).

[c] Dibutylurea and picric acid were dissolved together in alcohol, water was added and the oil which separated crystallized quickly on scratching.

[d] The oxalate precipitated when an alcohol solution of di-*iso*-amylurea was mixed with an aqueous solution of oxalic acid.

[e] Prepared by mixing an alcohol solution of di-iso-amylurea with an alcohol solution

of picric acid, diluting with water to precipitate the oil, dissolving the oil in alcohol, adding water to turbidity and allowing to stand. Melts at 72.8–73.9° with previous softening at 66.5–68°.

[f] The preparation was carried out in 50% alcohol because of the slight solubility of tetrahydroquinoline in water alone.

Purification of **α,α-Di-*n*-butylurea.**—The product separated as a yellow oil which floated upon the reaction mixture. The mixture was extracted with ether, and the ether extract was washed with dilute sulfuric acid for the removal of amine, then with water, dried with anhydrous sodium sulfate and concentrated in a vacuum over sulfuric acid. Attempts to distil the substance at ordinary pressure resulted in almost complete decomposition. It was distilled at a pressure of 2–3 mm. at 118–119°, and the distillate, although a water-white viscous oil of good appearance, smelled strongly of dibutylamine and was plainly less pure than before it had been distilled. The material was finally obtained pure by distilling it in the high vacuum (about 0.001 mm.) of a mercury diffusion pump. The tube containing the crude dibutylurea was sealed to two slender U-tubes (in series) each with a small bulb at the bottom of the U. The second U-tube was sealed to the pump. The tube containing the material and the U-tube nearest to it were then both warmed in an oil-bath at 50°, while the U-tube nearest the pump was cooled with liquid air. Dibutylamine distilled out and collected in white crystals in the cold tube. When no more amine could be collected, the tube containing the substance was heated in the oil-bath at 100–105°, and the U-tube directly connected to this was cooled in liquid air. The dibutylurea condensed in white needles which melted below room temperature to a colorless oil.

ω,ω-Di-*n*-propylbiuret.—In the preparation of dipropylurea, 30 g. of the amine and 40 g. of nitrourea were used. After the reaction was over, the mixture was extracted with ether and the ether extract was dried with solid caustic potash and concentrated. It yielded a residue which failed to crystallize after two weeks. On treating this with chloroform, 1.2 g. of insoluble material remained which was found to consist largely of urea along with a small amount of inorganic material. The chloroform solution desiccated in high vacuum gave 23.2 g. of white waxy needles of crude α,α-di-*n*-propylurea, and these extracted with petroleum ether yielded 0.5 g. of material insoluble in that solvent. Three recrystallizations from hot water made this material practically pure, m. p. 129°. It gave no biuret test or nitramine reaction and analyzed 22.28% of nitrogen; calcd. for $C_8H_{17}O_2N_3$, 22.46%. A mixed melting point showed it to be identical with the (slightly better) material, m. p. 129–129.4°, prepared from di-*n*-propylamine and nitrobiuret, and discussed more fully in the next paper of this series.

Preparation **of a-Alkyl-a-phenylureas.—The** reactions between nitrourea and mono-alkyl-anilines were carried out in the manner described in the first section of this paper.

TABLE III

α-ALKYL-α-PHENYLUREAS

Product	Yield, %	M. p., °C.	Remarks
a-Methyl-a-phenylurea	72	81.8–82.0	Thick prisms from benzene–ligroin
a-Ethyl-a-phenylurea	76	62.3–62.5	Thin plates from petroleum ether
a-n-Propyl-a-phenylurea	80	89.4–89.8	Thick plates and pyramids from benzene–ligroin. Nitrogen: found, 15.60; calcd. for $C_{10}H_{14}ON_2$, 15.73
Picrate	..	118–118.5	Needles from 50% alcohol. Nitrogen: found, 17.32; calcd. for $C_{16}H_{17}O_8N_5$, 17.19
Oxalate[a]	..	71–72	Recrystallized from 50% alcohol. Nitrogen: found, 12.37; calcd. for $(C_{10}H_{14}ON_2)_2 \cdot C_2H_2O_4$, 12.56
α-*n*-Butyl-α-phenylurea[b]	50	50.5–51.1	Waxy needles, very readily soluble in alcohol, ether and benzene. Nitrogen: found, 14.39; calcd. for $C_{11}H_{16}ON_2$, 14.58

[a] Softens at 65–66" and melts with decomposition at 71–72".

[b] a-n-Butyl-a-phenylurea separated from the reaction mixture as a dark-colored oil which did not respond to the usual devices for provoking crystallization but which crystallized spontaneously after standing for several months. The material was purified by treatment with decolorizing carbon and by repeatedly dissolving in alcohol and precipitating with water. The resulting pale yellow oil, dried in vacuum over sulfuric acid, was induced to crystallize by scratching. The substance is insoluble in water but very readily soluble in alcohol, benzene and ether, from all of which it is obtained as an oil.

The easy dearrangement of the a-alkyl-a-phenylureas may be demonstrated by heating a sample in a melting-point tube at 160–180°. The melt gradually deposits needles of cyanuric acid. The liquid portion consists of the free amine and does not solidify on cooling.

Effect of Heat on a-n-Propyl-a-phenylurea.—Three grams of the substance, heated in a distilling flask in the oil-bath, melted but showed no other change until a temperature of 210–215" was reached, when a sudden solidification took place. After a few minutes a liquid phase appeared above the solid one. The mixture, distilled in vacuum, yielded 2.15 g. of propylaniline, 94.3% of the theoretical. The residue in the flask weighed 0.78 g. and proved to consist of cyanuric acid.

ω-*n*-Propyl-ω-phenylbiuret.—The aqueous mother liquors from the preparation of propylphenylurea (from 50 g. of propylaniline) on evaporation to dryness yielded 2.8 g. of residue. All of this dissolved in 5 cc. of water, except 0.12 g. of material which was identified as cyanuric acid. The aqueous solution on dilution with alcohol deposited a small amount of inorganic matter and the liquid, concentrated and chilled, yielded 1.1 g. of small colorless glistening plates, m. p. 150–151°. Two recrystallizations from alcohol raised the melting point to 151°. The material gave no biuret test or nitramine reaction and analyzed 19.14% of nitrogen; calcd. for $C_{11}H_{15}O_2N_3$, 19.00. A mixed melting point showed it to be identical with the (slightly better) material, m. p. 151–151.5°, prepared from propylaniline and nitrobiuret.

Summary

Nitrourea dearranges into cyanic acid and nitroamide. It has been prepared from these two substances, and they have been prepared from it.

The products from the decomposition of nitrourea by heat are those which would be expected from the two possible modes of its dearrangement.

Nitrous oxide and cyanic acid are produced quantitatively when nitrourea is heated with water.

A solution of nitrourea in concd. sulfuric acid contains nitroamide and may be used as a reagent for nitrations.

Alkalies promote the decomposition of nitrourea; acids hinder it. A very slight alkalinity in the presence of a trace of moisture is sufficient to cause its spontaneous decomposition.

An aqueous solution of nitrourea, being a source of cyanic acid, reacts with ammonia and with primary and secondary amines to form urea and substituted ureas. The yields are excellent, the manipulation is simple and the other products of the reaction are gaseous. The method is especially advantageous for the preparation of those substituted ureas which cannot be heated in water without decomposition. A number of urea derivatives, a few of them new, have been prepared by this method.

ω,ω-Di-*n*-propylbiuret and ω-*n*-propyl-ω-phenylbiuret have been obtained as by-products in the preparation of urea derivatives from nitrourea and the corresponding amines.

Moist alcohols react with nitrourea to produce carbamic and allophanic esters.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 39 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE DEARRANGEMENT OF NITROBIURET AND ITS APPLICATION IN SYNTHESIS

BY TENNEY L. DAVIS AND KENNETH C. BLANCHARD

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

A study of the dearrangement of nitrobiuret is especially interesting for the reason that it might be expected to produce the unknown dimer of cyanic acid, dicyanic acid, NH_2CONCO (or HOC(NH)-NCO). Nitrobiuret might be expected to dearrange in four modes, as indicated below. The known or expected decompositions of the nitro-amines from the four modes of dearrangement are also shown.

$$NH_2CONHCONHNO_2 \rightleftharpoons NH_2CONCO + NH_2NO_2 \longrightarrow N_2O + H_2O \quad (1)$$

$$NH_2CONHCONHNO_2 \rightleftharpoons NH_2CONH_2 + OCNNO_2 \longrightarrow N_2O + CO_2 \quad (2)$$

$$NH_2CONHCONHNO_2 \rightleftharpoons NH_3 + OCNCONHNO_2 \longrightarrow N_2O + CO_2 + HNCO \quad (3)$$

$$NH_2CONHCONHNO_2 \rightleftharpoons HNCO + NH_2CONHNO_2 \longrightarrow N_2O + H_2O + HNCO \quad (4)$$

We find that a freshly prepared cold aqueous solution of nitrobiuret does not give the biuret test. If the solution is boiled, nitrous oxide and carbon dioxide come off, and the liquid now gives a strong biuret test but shows no evidence of cyanic acid by Werner's sensitive test with copper sulfate, pyridine and chloroform. The solution, however, contains no biuret, for it yields a residue of urea along with some cyanuric acid when it is evaporated to dryness. Although the boiled solution at the beginning does not contain cyanic acid, it develops cyanic acid during the evaporation—but this is normal behavior of urea solutions. Since the solution immediately after dearrangement does not contain cyanic acid, we conclude at once that dearrangements of the third and fourth sorts (as indicated above) do not occur.

The evolution of nitrous oxide and carbon dioxide from the hot solution and the production of urea, as originally observed by Thiele and Uhlfelder,[1] suggest strongly that dearrangement occurs in the second of the above-indicated modes. The biuret test in the absence of biuret indicates some other reaction—and is, we believe, evidence of the presence of dicyanic acid in the solution. Moreover, solutions of nitrobiuret act with ammonia, amines and alcohols as if they contained dicyanic acid and yield with those reagents the products which that substance would be expected to yield. We conclude, therefore, that dearrangement occurs in the first two modes, namely, to form nitroamide and dicyanic acid, and urea and nitrocyanic acid.

A solution of nitrobiuret in concd. sulfuric acid gives up its nitro group quantitatively in the nitrometer and is a suitable reagent for the nitration of substances such as aniline and acet-p-toluide which are not injured by contact with strong sulfuric acid.

Nitrobiuret with alcoholic potash yields potassium allophanate. By boiling with alcohols and a little water, it produces allophanic and carbamic esters.

With ammonia it yields biuret along with some cyanuric acid and urea. With primary and secondary amines it gives ω-substituted biurets, substances which are evidently produced by the direct combination of the amine with dicyanic acid, thus

$$R_2NH + NH_2CONCO \longrightarrow NH_2CONHCONR_2$$

In this manner we have prepared ω-methyl-, ω-ethyl-, ω-n-propylbiuret (new), ω-*n*-butylbiuret (new), ω-benzylbiuret (new), ω-phenyl-, ω-*p*-tolyl-, and ω-α-naphthylbiuret (new), and from secondary amines a number (all new) of ω,ω-disubstituted biurets, namely, ω,ω-dimethyl-, ω,ω-diethyl-, ω,ω-di-n-propyl-, ω,ω-di-*n*-butyl-, ω-ethyl-ω-phenyl- and ω-*n*-propyl-ω-phenylbiuret.

The dicyanic acid from the dearrangement of nitrobiuret in water solu-

---

[1] Thiele and **Uhlfelder,** *Ann.,* **303, 93** (1898).

tion does not combine with urea to form carbonyldiurea or triuret,[2] but does combine with biuret to form tetruret.

Experiments

Preparation of Nitrobiuret.—Nitrobiuret was prepared by a method essentially that of Thiele and Uhlfelder.[1] Our first crude product from the drowning of the nitration mixture, purified by dissolving it in water with the addition of sodium hydroxide and precipitating with hydrochloric acid, yielded, from 100 g. of biuret with water of crystallization, 95 g., 70% of the theoretical, of very small white crystals which decomposed at 175–180°. Thiele and Uhlfelder report a decomposition temperature of 165". Two recrystallizations from water (52 cc. per gram) at 65–67° raised the decomposition temperature to 223". It was found necessary to carry out the crystallization below 70°, for at that temperature the solution begins to decompose with the evolution of gas. The nitrobiuret was identified by conversion to benzalaminobiuret and by analysis with the nitrometer; nitro group nitrogen: found, 9.50, 9.37; calcd. for $C_2H_4O_2N_3NO_2$, 9.42.

Tests for Nitrobiuret.—Nitrobiuret gives no color with ferrous sulfate and sodium hydroxide solution, in which respect it differs from nitroguanidine.8 One-tenth of a gram of nitrobiuret in 5 cc. of water, treated with 1 *g.* of zinc dust and 1 cc. of 50% acetic acid, allowed to stand for fifteen minutes, and filtered, yielded a solution which did not reduce silver acetate in the cold (as does the corresponding solution from nitroguanidine) but reduced ammoniacal silver nitrate instantly. When a small drop of benzaldehyde was added to such a solution, a crystalline precipitate of benzalaminobiuret was formed within a few minutes.

Decomposition of Nitrobiuret in Aqueous Solution.—Portions of about 1 g. each of nitrobiuret were dissolved in 10 cc. of water, warmed until gassing ceased and evaporated to dryness on the water-bath. The weight of residue in several experiments varied between 44.8 and 47.2% of the weight of the nitrobiuret which was taken. About 80% of the residue consisted of urea; about 20% of cyanuric acid. No other substance was found.

Nitrations with Nitrobiuret.—A solution of 3 g. of nitrobiuret in 30 cc. of concd. sulfuric acid at 2–3° was added slowly and with stirring to a cold solution of 1.96 g. of aniline in 7 cc. of concd. sulfuric acid. The mixture was stirred continuously for six hours while cooled with ice, then poured onto cracked ice, made alkaline with ammonia and extracted with chloroform. The chloroform solution yielded 2.34 g. of mixed nitranilines, 85% of the theoretical. This was analyzed by the melting-point method of Holleman, Hartogs and van der Linden[4] and found to consist of 30.3% *p*-, 42.0% o- and 27.7% m-nitraniline.

Three grams of nitrobiuret in 30 cc. of concd. sulfuric acid and 3 g. of acet-*p*-toluide in 10 cc. were mixed and warmed in the boiling water-bath for fifteen minutes. The mixture was drowned in ice water and the product, recrystallized from water, gave 1.5 g. of m-nitro-acet-p-toluide as pale yellow needles, m. p. 94–94.3°.

Potassium Allophanate from Nitrobiuret.—Five and six-tenths grams of nitrobiuret and 2 g. of potassium hydroxide were refluxed together for two hours in 60 cc. of 80% alcohol. Small plates of potassium allophanate separated from the cold liquid. These, after washing with alcohol and ether, weighed 0.95 g., 32% of the theoretical.

---

[2] Cyanic acid from nitrourea in water solution does not combine with urea to form biuret. A solution of urea and nitrourea on evaporation to dryness yields only urea along with some cyanuric acid and ammonium cyanurate.

[3] Davis, Ashdown and Couch, THIS JOURNAL, 47,1063 (1925).

[4] Holleman, Hartogs and van der Linden, *Ber.*, 44, 704 (1911).

The material was recrystallized from alcohol and a portion of it was converted to potassium sulfate by evaporation with sulfuric acid; 0.4632 g. yielded 0.5637 g. of K_2SO_4; calcd. for $C_2H_3O_3N_2K$, 0.5676.

In a similar experiment with absolute alcohol, no potassium allophanate was obtained. The fact that no gas was given off showed that dearrangement did not take place in the anhydrous solution.

In an experiment with 50% alcohol, urea was produced but no potassium allophanate could be isolated. The dicyanic acid was apparently hydrolyzed.

Reaction with Alcohols.—Portions of nitrobiuret were refluxed, respectively, with absolute ethyl, absolute n-propyl, absolute n-butyl and absolute *tert.*-butyl alcohols. The nitrobiuret was recovered unchanged and no evidence was found of carbamic or allophanic ester.

When nitrobiuret was refluxed with a 1% solution of water in the various alcohols, dearrangement evidently occurred, for nitrous oxide was evolved. The solutions were evaporated to dryness and the residues were extracted with boiling aviation gasoline and with boiling benzene, but neither of the extracts contained any dissolved substance—and we conclude that no carbamate or allophanate was formed. The material insoluble in gasoline and benzene was found in each case to be urea and cyanuric acid.

Five cc. of the alcohol and 1.4 g. of nitrobiuret in a small flask under reflux were heated in the boiling water-bath until no more air was driven out of the apparatus. Water was then admitted through a dropping funnel until the evolution of nitrous oxide commenced. The heating was continued for fifteen or twenty minutes until gas production had ceased. The solutions were evaporated to dryness; the residues were dried in vacuum and extracted with hot gasoline and hot benzene. The resulting carbamates and allophanates were identified, after recrystallization, by mixed melting points with samples of known purity. The yields are tabulated below.

TABLE I

PRODUCTS (GRAMS) FROM 1.4 GRAMS OF NITROBIURET AND 5 CC. OF ALCOHOL

Alcohol	Ethyl	n-Propyl	n-Butyl	*Tert.*-butyl	*Iso*-amyl
Carbamate	0.05	0.10	0.13	0.16	None
Allophanate	0.23	0.12	0.30	None	0.25

The carbamates are not formed first, for nitrobiuret does not dearrange to produce cyanic acid which could form them directly by combination with the alcohols. Undoubtedly the dicyanic acid from the dearrangement first combines with the alcohols to form allophanates, and these react with the alcohols to produce carbamates. We have found in fact that allophanates are converted to carbamates by reflaxing with alcohols.

Reaction with Ammonia.—Twenty-five cc. of strong ammonia water and 1.4 g. of nitrobiuret, heated together in a sealed tube at 100° for four hours, yielded 0.7 g. of biuret, 60% of the theoretical, and small amounts of cyanuric acid and urea.

Substituted Biurets.—Nitrobiuret and an equivalent quantity of the amine were brought together in water, generally enough to dissolve both reagents, and the mixture. was warmed gently until gas evolution had ceased. The liquid was then refluxed for fifteen or twenty minutes and allowed to cool for crystals—or concentrated and cooled—or evaporated to dryness, in which case the substituted biuret was extracted with an organic solvent which did not dissolve the cyanuric acid. All of the products were recrystallized to constancy of melting point; yields, etc., are shown in Table II.

The low yields in the cases of methyl- and ethylbiuret are evidently due to loss of the amines by volatilization. An experiment in which nitrobiuret, methylamine and water

TABLE II

SUBSTITUTED BIURETS

Substance, -biuret	Yield, %	% Nitrogen, Found	% Nitrogen, Calcd.	M. p., °C.	Habit
ω-Methyl	12.5	...	...	166.5–167	Prisms from alcohol
ω-Ethyl	23.9	...	...	154–154.5	Fine needles from alcohol
ω-*n*-Propyl	45.0	27.67	27.58	147.2–147.6	Recrystallized from water
ω-*n*-Butyl	70.0	26.33	26.41	129.1–129.5	Irregular shiny plates from water
ω-Benzyl	43.0	21.33	21.24	174 5–175	Tufts of microscopic prisms from water
ω-Phenyl	80.0	...	...	165	Silky needles from water
ω-*p*-Tolyl	62.0	...	...	199	Fine needles from water
ω-α-Naphthyl	52.0	18.28	18 34	217.3–217.6	Very fine needles from 50 per cent. alcohol
ω,ω-Dimethyl	33.6	32 18	32.06	141–141 5	Thick needles from water
ω,ω-Diethyl	80.0	26 50	26.41	139–139.2	Thick pointed leaflets from water
ω,ω-Di-*n*-propyl	62.0	22.54	22.46	129–129 4	Fine sharp needles from water
ω,ω-Di-*n*-butyl	50 0	19.37	19.53	144 8–145	Small glistening plates from water
ω-Ethyl-ω-phenyl	71.0	20.41	20.29	155.2–155.8	Thin glistening plates from alcohol
ω-*n*-Propyl-ω-phenyl	45.3	18.96	19 00	151–151.5	Thin glistening rectangular plates from alcohol

were heated in a sealed tube at 100° for half an hour gave a yield of 50% of the theoretical amount of ω-methylbiuret.

Nitrobiuret and Urea.—Two and eight-tenths grams of nitrobiuret and 1.2 g. of urea were dissolved in 25 cc. of water, allowed to stand for several days, diluted to 50 cc. and heated to boiling. On evaporation to 10 cc. and cooling, the mixture deposited crystals which did not melt at 260° and were identified as cyanuric acid. Schiff[5] reports that carbonyldiurea melts at 231–232° and is only sparingly soluble in water.

Nitrobiuret and Biuret. Tetruret.—One and four-tenths grams of nitrobiuret and 1 2 g. of biuret were dissolved in 50 cc. of warm water. After gassing had ceased, the mixture was evaporated to 10 cc. Six-tenths of a gram of crystals separated, m. p. 178–180°. Two recrystallizations from water raised the melting point to 186 2–187.1°. When treated with the reagents for the ordinary biuret test, the substance gave a beautiful blue-violet color such as Thiele and Uhlfelder[1] had found to be characteristic of tetruret. Those workers had prepared the substance by the action of ammonia on allophanic acid azide and reported the melting point as 186°.

Summary

Nitrobiuret appears to dearrange in two modes, to form nitroamide and dicyanic acid, and nitrocyanic acid and urea. When an aqueous solution is warmed, the nitroamide evidently breaks down into nitrous oxide and water, the nitrocyanic acid into nitrous oxide and carbon dioxide, and the liquid acts toward various reagents as if it contained dicyanic acid.

---

[5] Schiff, Ann., 291,374 (1896).

With moist alcoholic potash nitrobiuret yields potassium allophanate.

With moist alcohols it gives allophanic esters which react with the alcohols on refluxing to produce carbamic esters.

With aqueous ammonia it yields biuret; with biuret, tetruret; with primary and secondary amines, w-substituted biurets.

A number of w-mono-substituted biurets (several new) and of ω,ω-di-substituted biurets (all new) have been prepared and are described.

A solution of nitrobiuret in concd. sulfuric acid gives up its nitro group quantitatively in the nitrometer and is a suitable reagent for nitrations.

CAMBRIDGE, MASSACHUSETTS

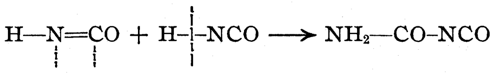
[CONTRIBUTION NO. 40 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

DICYANIC ACID

BY TENNEY L. DAVIS AND KENNETH C. BLANCHARD

RECEIVED JANUARY 5, 1929 PUBLISHED JUNE 5, 1929

Cyanamide, which differs from cyanic acid in having an NH group in place of an oxygen atom, combines with itself in warm water solution, one molecule functioning as a derivative of cyanic acid and one as a derivative of ammonia, to form a dimer which is a urea derivative, namely, dicyandiamide or cyanoguanidine. When heated in the dry state cyanamide trimerizes to form melamine, a white crystalline solid, sparingly soluble in cold water, which sublimes without melting. Cyanic acid yields a similar trimer, cyanuric acid, of about the same physical properties as melamine. We have found evidence which shows that cyanic acid in solution dimerizes in part, one molecule evidently functioning in the usual manner of cyanic acid in urea formation and one as an ammonia derivative, namely, as carbonyl-ammonia, to form a urea derivative, carbonylurea or dicyanic acid.



$$\mathrm{H{-}N{=}CO + H{-}NCO \longrightarrow NH_2{-}CO{-}NCO}$$

Dicyanic acid gives the biuret test; cyanic acid does not. Cyanic acid combines with amines to yield urea derivatives; dicyanic acid with amines to form biuret derivatives. An aqueous solution of cyanic acid in which some dimerization has occurred gives with aniline both phenylurea and phenylbiuret. With alcohols it yields both carbamic and allophanic esters.

Cyanic acid behaves in several different ways in aqueous solution. (1) It ionizes as a weak acid. (2) It trimerizes to cyanuric acid, which may precipitate out or may appear as a residue when the liquid is evaporated. (3) It undergoes hydrolysis to produce ammonia and carbon dioxide, and the ammonia combines with unchanged cyanic acid to form urea and ammonium cyanate in the ratio corresponding to the equilibrium between these substances. (4) It dimerizes to form dicyanic acid.[1] Dicyanic acid either depolymerizes during the evaporation of the solution or undergoes hydrolysis—for an aqueous solution of cyanic acid yields only urea and a little cyanuric acid when it is evaporated to dryness.

The dimerization of cyanic acid is obviously due to the affinity of one molecule of cyanic acid for another molecule of the same kind. Different solvents would probably have different effects upon it, some causing more dimerization or association, some less. The affinity of cyanic acid for the solvent itself would also come into play. Thus, cyanic acid gas passed into a solvent which has a great affinity for it would react with the solvent and might not dimerize at all. Passed into a solvent for which it has little or no affinity, it would be more likely to dimerize. When cyanic acid gas is passed into an alcohol, one portion may combine with the alcohol to form a carbamic ester, another portion may dimerize to form dicyanic acid which then combines with the alcohol to form an allophanic ester. Evidently the associating action of the solvent and the relative affinities of cyanic acid for cyanic acid and of cyanic acid for the solvent are both to be considered. These matters are now under investigation in this Laboratory.

The formation of allophanic ester from cyanic acid and alcohol was long ago explained by Hofmann[2] as being due to the direct combination of one molecule of cyanic acid with one of alcohol to produce carbamic ester and to the subsequent addition of a second molecule of cyanic acid to this substance. He claimed indeed to have prepared allophanic ester by the action of cyanic acid on urethan. Béhal[3] more recently was unable to obtain any allophanic ester by this method. He prepared an extensive series of aliphatic and aromatic allophanates by passing into the corresponding alcohols cyanic acid gas from the thermal depolymerization of cyanuric acid.[4] Carbamates were formed at the same time. He supposed that the allophanates probably resulted from the combination of the alcohols with dicyanic acid produced during the depolymerization. We think it more likely that the dicyanic acid is produced by dimerization in the liquid phase—and have found that the cyanic acid which results from the acidification of a solution of potassium cyanate dimerizes in part and yields both carbamic and allophanic esters with alcohols.

Lane[5] refluxed urea with n-butyl alcohol for three hours and obtained both allophanate and carbamate. After six hours' boiling he found only carbamate. He heated n-butyl carbamate with urea and with nitrourea,

---

[1] The dimer of phenylisocyanate has been prepared by Hoffmann, *Ber.*, 4, **246** (1871), by the action of triethylphosphine on phenylisocyanate, and by Snape, *Trans. Chem. Soc.*, **49**, **254** (1886), by the action of pyridine.

[2] Hofmann, *Ber.*, **4**, 268 (1871).

[3] Béhal, *Bull. soc. chim.*, *25*, 477 (1919).

[4] Liebig and Wöhler, *Ann.*, **39**, 29 (1846).

[5] Lane, Bachelor's "Thesis," Massachusetts Institute of Technology, 1925.

and failed to produce any allophanate. Bishop[6] obtained both allophanate and carbamate by refluxing n-butyl alcohol with biuret for a short time, and on longer refluxing less of the allophanate. We conclude that the allophanate is formed directly and independently of the carbamate, and hence that dicyanic acid is present in the solution.

Carbamic ester when heated in alcohol solution evidently dissociates in part, reversing its formation from cyanic acid and alcohol. The cyanic acid which results associates in part to form dicyanic acid, which then combines with the alcohol to form allophanic ester. By heating ethyl carbamate with alcohol in a sealed tube at 100° we have converted a portion of it into ethyl allophanate.

An aqueous solution of potassium cyanate in a warm room hydrolyzes rapidly and contains both cyanic acid and urea. We have isolated urea from such a solution. The liquid however fails to give a biuret test, even after standing for several hours. It is evident that cyanic acid and urea do not combine to form biuret under these conditions.

When a concentrated aqueous solution of potassium cyanate is acidified with acetic acid and allowed to stand for a few minutes, the resulting liquid gives a biuret reaction. Werner[7] supposes that a portion of the cyanic acid undergoes hydrolysis, that urea is formed and that this combines with cyanic acid to form biuret. We find that the solution contains no biuret. By a colorimetric method the amount of biuret necessary to give a biuret reaction of the observed intensity was determined. The solution was worked up for biuret and none was found. An amount of actual biuret corresponding to the colorimetric determination was added to a similar solution; the liquid was worked up for biuret and four-fifths of that which had been added was recovered. An acidified solution of potassium cyanate, after standing for a short time, gave with aniline both phenylurea and ω-phenylbiuret.

The aqueous solutions which result, respectively, from the passage of cyanic acid (from the depolymerization of cyanuric acid) into water, and from warming a solution of nitrourea until gas evolution ceases, both give the biuret test. They contain cyanic acid and dicyanic acid—and, after standing, urea—but contain no biuret and yield on evaporation residues which consist of urea along with a little cyanuric acid. The liquid which results from warming an aqueous solution of nitrobiuret contains at first dicyanic acid but no cyanic acid; it gives the biuret test and yields a similar residue on evaporation.

Experiments

Allophanates and Carbamates from Potassium Cyanate.—Thirty cc. of ethyl alcohol was added to a solution of 16.2 g. of potassium cyanate in 30 cc. of water; the mixture

---

[6] Bishop, Bachelor's "Thesis," Massachusetts Institute of Technology, 1925.

[7] Werner, "The Chemistry of Urea," London, 1923, p. 26.

was acidified with hydrochloric acid, allowed to stand for an hour and evaporated to dryness. The residue was extracted first with aviation gasoline and then with benzene, and the extracts yielded, respectively, 0.3 g. of ethyl carbamate, m. p. 49–50" after sublimation, and 1.4 g. of ethyl allophanate. m. p. 197–198° after recrystallization from benzene, both further identified by mixed melting points with known samples.

Similar experiments with 0.2 mole of potassium cyanate, 25 cc. of water and 0.1 mole of n-butyl and of iso-amyl alcohol yielded, respectively, 0 2 g. of n-butyl carbamate, m. p. 51–52", and 0.4 g. of n-butyl allophanate, m. p. 149–149.5°; and 0.3 g. of *iso*-amyl carbamate, m. p. 64–65° after sublimation and 0.1 g. of *iso*-amyl allophanate, m. p. 161.8–162.5°.

Ethyl Allophanate from Ethyl Carbamate.—Several experiments were tried in which urethan was refluxed for different intervals of time with different amounts of alcohol, but no allophanate was found in the residues when the liquids were evaporated to dryness. It was believed that whatever cyanic acid may have been produced escaped through the condenser. Ten cc. of alcohol was therefore heated with 8.9 g. of urethan in a sealed tube at 100° for half an hour. The residue from the evaporation of the liquid yielded 0.4 g. of material insoluble in gasoline which was identified as ethyl allophanate by mixed melting point.

The Biuret Test in an Acidified Solution of Potassium Cyanate.--Six cc. of glacial acetic acid was added very slowly to a well-stirred solution of 8.1 g. of potassium cyanate in 20 cc. of water. The mixture was brought to neutrality with barium carbonate, filtered and diluted to 50 cc. The intensity of color in the biuret reaction of a 5-cc. portion of this liquid was found to be equal to that produced by 0.03 g. of actual biuret—which would correspond to 0.27 g. of biuret in the remaining 45 cc. of solution. The remaining solution was evaporated to dryness and the residue was refluxed with 5 cc. of alcoholic potash (in which biuret is soluble while cyanuric acid is almost insoluble). The filtrate, acidified with hydrochloric acid and filtered for the removal of potassium chloride, was evaporated to a small volume. This solution gave no biuret reaction and on chilling in a freezing mixture deposited a few crystals of potassium acetate. Three repetitions of the experiment gave identical results. A similar experiment, in which 0.3 g. of actual biuret was added to the water in which the potassium cyanate was dissolved, gave a final residue which gave the biuret reaction with an intensity of color which corresponded to 0.24 g. of biuret or four-fifths of the amount which had been added.

Phenylbiuret from Potassium Cyanate.—A solution of 8.1 g. of potassium cyanate in 25 cc. of water was chilled and acidified with 6 cc. of glacial acetic acid. After five minutes, 9.3 g. of aniline was added. The mixture was stirred for five minutes, diluted with 100 cc. of hot water, filtered, freed from excess aniline and refluxed for two hours to convert the phenylurea into insoluble carbanilide. The filtrate on chilling yielded silky needles of phenylbiuret along with a small quantity of phenylurea. The product, recrystallized from water, amounted to 0.6 g., 3.3% of the theoretical, of ω-phenylbiuret, m. p. 165°.

Summary

Chemical evidence is presented which shows that cyanic acid in solution dimerizes in part to form dicyanic acid.

Allophanic esters and biuret are formed directly from the alcohols and from ammonia, respectively, not by the addition of cyanic acid to intermediate carbamic esters and urea.

Aqueous solutions of cyanic acid contain some substance, not biuret,

which gives a biuret test, which reacts with aniline to form phenylbiuret and with alcohols to form allophanic esters.

CAMBRIDGE, MASSACHUSETTS

[COMMUNICATION NO. 377 FROM THE KODAK RESEARCH LABORATORIES]

EFFECT OF ANILINE ON CELLULOSE TRIACETATE

BY H. LEB. GRAY, T. F. MURRAY, JR., AND C. J. STAUD

RECEIVED JANUARY 8, 1929 PUBLISHED JUNE 5, 1929

Introduction

The action of aniline and similar compounds on cellulose triacetate has been studied but little by investigators in the field of cellulose chemistry. In a paper by E. Knoevenagel,[1] published in 1914, however, mention is made that triacetylcellulose may be heated with aniline without saponification of the ester. It is pointed out that marked differences in solubility result, which the author ascribes as possibly due to a stereoisomeric change of the cellulose acetate molecule, similar to that which produces mutarotation in the sugars. No polarimetric data are given.

That an ester like cellulose acetate could be kept in contact with a base like aniline at a high temperature for a protracted period of time without saponification seemed somewhat incongruous. Therefore, a study was made of the effect of aniline at various temperatures on cellulose triacetate.

Experimental

General Procedure.—The general procedure employed in these experiments was as follows. Fifteen grams of finely-divided cellulose acetate, containing 43.9% of acetyl (theoretical cellulose triacetate, 44.8% acetyl), and 300 cc. of aniline (b. p. 88–90' at 15 mm.) were placed in a 500-cc. ring-necked Pyrex flask equipped with an air condenser.

Three series of experiments were made. The first of these at the boiling point of the aniline–cellulose acetate solution (approx. 183°) was done in an oil-bath, the solution being refluxed continuously. The second at 148–151" was carried out by placing the flask in an air-bath, the temperature of which was maintained by the vapors of boiling cyclohexanol (b. p. 157–162°) and the third series was conducted at room temperature, 20–25°.

In the series in which elevated temperatures were employed, the solutions were cooled to approximately zero degrees and the mixtures were poured into 3 liters of ethyl alcohol. The products were washed with alcohol until free from aniline; this was followed by washing with ether. They were dried at 35°, after which the samples for analyses were dried at 105" for fifteen to twenty hours. Acetyl determinations were made according to the method of Eberstadt[2] as described by Knoevenagel,[3] with slight modifications. Optical rotations were determined using a Hilger polarimeter (accuracy 0.01") employing the 546.1 mμ line of the mercury spectrum as illuminant. Readings

---

[1] Knoevenagel, Z. *angew. Chem.*, **27**, 505 (1914).

[2] Eberstadt, "Dissertation," Heidelberg, 1909.

[3] Knoevenagel, *Cellulosechemie*, **3**, 119 (1922).

were made at 25 ± 1°, in a 2-dm. tube. The concentration was 1% in chloroform–alcohol (85:15% by volume) and where possible in acetone.

Heating at 183°.—In Table I are given the results of the first series of experiments in which the aniline–cellulose acetate solutions were heated at the boiling point.

TABLE I

RESULTS AT 183°

Time, hours	Product recovered, g.	Equiv. wt of cellulose, g.	CH_3CO— in prod., %	$(\alpha)^{25°}_{546.1}$, $CHCl_3-EtOH$	$(\alpha)^{25°}_{546.1}$, acetone
0	..	8.4	43.9	−26.0	
1	14.4	8.2	43.4	−26.0	
2	16.0	9.1	43.0	−26.0	
2	15.1	8.7	42.3	−24.5	
4	16.3	9.3	42.7	−25.0	
6	14.1	8.2	42.1	−21.5	
6	14.1	8.2	42.1	−21.5	
8	14.4	8.4	41.6	−20.0	+ 2.0
10	13.1	7.9	40.0	−15.5	+ 4.5
15	12.9	7.9	39.0	−12.5	+ 5.5
20	12.1	7.7	36.1	− 8.0	+10.0
25	10.5	7.5	28.5	Insol.	Insol.
30	10.0	7.4	26.5		
40	9.8	8.1	17.7		
50	8.7	8.0	7.9		
50	8.7	7.9	8.7		
75	8.5	8.1	4.4		
100	8.5	8.4	1.5		
100	7.9	7.7	2.3		
		Av. 8.2			

From the above table it is seen that cellulose acetate is saponified by heating with aniline at the boiling point of the aniline–cellulose acetate solutions. This is shown graphically in Curve A of Fig. 1. The decrease in acetyl content is apparent after as short a time as two hours. After one hundred hours of heating, the acetyl content had decreased to 2.0%. The weight of the recovered material affords evidence that no appreciable hydrolysis to alcohol- or ether-soluble products, such as acetylated sugars, has taken place. The theoretical yield of cellulose obtainable from the saponification of 15 g. of cellulose acetate containing 43.9% acetyl is 8.4 g. If the weights of recovered cellulose acetate, after various times of heating, be calculated back to their cellulose contents, by multiplying the weight of recovered acetate by the percentage of cellulose which they contain (100 − % acetyl),[4] values between 7.4 and 9.1 grams are obtained.

---

[4] The value given does not rigorously represent the cellulose content since the CH_3CO removed would be replaced by an equivalent weight of hydrogen. Such calculation, however, is quite outside the accuracy of these experiments. It does not affect the results by more than 0.2 g. of cellulose.

The average recovered material, calculated to cellulose, is 8.2 g., which shows very acceptable agreement with this theoretical value, as does the material which has been almost completely saponified (2.0% acetyl) by heating with aniline for one hundred hours, the latter value being 8.2 g.

To test further the action of aniline on the product obtained after one hundred hours' heating, a 5-g. sample of this material was heated for an additional one hundred hours in 300 cc. of aniline at its boiling point. The material did not dissolve and at the end of the second one hundred hours of heating, 4.6 g. of material was recovered. On analysis this showed an acetyl content of 1.3%.

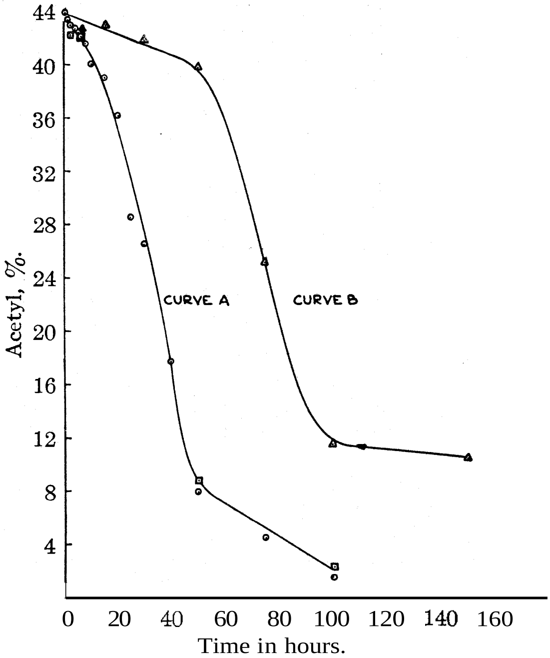


Fig. 1.—Acetyl content of cellulose acetate heated with aniline *vs.* time of heating.

According to Knoevenagel profound changes in the solubility of cellulose acetate are induced by the action of aniline, which he ascribes to stereoisomerism. It has been found that changes in solubility do take place, but they appear to follow the normal course observed in the saponification of cellulose acetate. In the experiments described it was observed that the cellulose acetate obtained, after heating with aniline for eight hours, was soluble in acetone and in a solution consisting of 85% chloroform and 15% ethyl alcohol by volume. After twenty-five hours' heating, the material obtained was practically insoluble in acetone and not entirely soluble in the chloroform-alcohol mixture mentioned above, but soluble in hot 75% ethyl alcohol. At the end of thirty hours' heating the product was soluble in aniline but not in the other solvents mentioned, and at the close of forty hours' heating it became insoluble, even in boiling aniline.

For the purpose of determining whether the final product of aniline saponification was cellulose or one or more of its decomposition products, **5** g. of the material obtained after one hundred hours' heating with aniline was reacetylated and **7.8** g. of a compound was obtained (theoretical for cellulose triacetate **8.9** g.) which contained 44.2% of CH_3CO (theoretical for cellulose triacetate, **44.8%)** and had a specific rotation of $-26.0°$, which is the same value as that of the starting material.

Heating at 148–151°.--To determine the difference in rate of saponification of cellulose acetate by aniline resulting from a change in temperature, a series of experiments was made at 148–151°, for a maximum time of 150 hours. At the close of this period the rate of hydrolysis had become very low. The data obtained are given in Table II.

TABLE II

RESULTS AT 148–151°

Time, hours	Product recovered, g.	Equiv. wt. of cellulose, g.	CH_3CO in prod., %	$(\alpha)^{25°}_{546.1}$, $CHCl_3-EtOH$	$(\alpha)^{25°}_{546.1}$, acetone
0	..	**8.4**	43.9	**−26.0**	
6	14.9	**8.4**	42.6	**−23.5**	
15	13.6	**7.8**	43.0	**−24.5**	Insol.
30	13.6	**7.9**	41.9	**−20.0**	(0.0)
50	12.7	**7.7**	39.8	**−16.0**	+2.0
75	9.7	**7.3**	25.2	Insol.	Insol.
100	9.2	**8.2**	11.5		
150	9.0	**8.1**	10.4		
		Av. **8.0**			

The decrease in acetyl content with time of heating is shown in Curve B of Fig. 1. It is seen to be of the same form as that obtained at the higher temperature. It appears of interest to note that both curves exhibit an S-form, in which the saponification is slow at the start, increasing during the intermediate stages with a marked decrease in the rate toward the close.

A calculation of the cellulose equivalent of the various cellulose acetates obtained in this series varied from 7.3 to 8.4 g., with an average of 8.0 g., which shows good agreement with the theoretical value of 8.4 g. previously mentioned, as well as with the yields obtained in the first series.

Effect of Standing at 20–30°.—Since in each experiment of the above two series the contents of the reaction flask were allowed to cool to room temperature and permitted to stand at that temperature for irregular periods of time before being poured into alcohol, a check on the action of aniline on cellulose acetate at room temperature seemed necessary to establish the validity of the results obtained at higher temperatures.

A 15-g. sample of the same cellulose acetate that was used in the previous experiments, therefore, was placed in **300** cc. of aniline and the containing flask was heated in a 148–151° bath for one hour. At the end of this time all of the cellulose acetate had dissolved. The solution was then allowed to stand at room temperature, and twenty-five hours after removal from the bath, a portion was precipitated in ethyl alcohol, washed with alcohol, dried and analyzed. The acetyl content was found to be 43.5%, and the specific rotation in chloroform–alcohol (85:**15)** was **−26.5". The** remainder of the solution was permitted to stand at room temperature for an additional 125 hours. It was then precipitated, washed and dried in a similar manner, and upon analysis gave the following values: acetyl content 43.2%; specific rotation, chloroform–alcohol (85:15) −25.5°. The difference between these values and those of the original cellulose acetate of 43.9% acetyl, and specific rotation of −26.0°, is so slight that it appears that no appreciable changes have taken place during the 150 hours' standing at room temperature. Since this time is far in excess of that during which any of the samples was permitted to stand before precipitation, it is concluded that the validity of this procedure is established and also that the deesterifying action of aniline on cellulose acetate at room temperature is exceedingly slow.

Discussion of the **Polarimetric** Data.—From the data given in the tabulations, it is obvious that there is a continuous decrease in specific rotation in chloroform–alcohol, within its solubility range, of the products obtained after various periods of heating in aniline, and conversely a progressive increase in specific rotation in acetone of the products which are soluble in this reagent.

If the phenomenon of change of solubility were one of stereoisomerism, comparable with the mutarotation of the sugars, from the definition of mutarotation,[5] a "steady state" should be found. The polarimetric data fail to indicate any such "steady state" and, in fact, since the acetyl values change continuously during the heating, a simultaneous change in optical rotation might be expected.

Summary

1. The effect of aniline on cellulose acetate has been investigated at room temperature and two higher temperatures.
2. The acetyl contents and specific rotations, where possible, have been determined on the products.
3. It has been found that the cellulose equivalent of all the products agrees approximately with the theoretical value.
4. Contrary to Knoevenagel, it has been observed that there is a continuous decrease in acetyl content with time of heating.
5. The specific rotations, so far as present interpretation permits, do not seem to indicate the possibility of a stereoisomeric change comparable with the mutarotation of the sugars, as suggested by Knoevenagel.
6. The product obtained by prolonged saponification with aniline at 183° is shown to contain approximately 2% of acetyl, and upon reacetylation to revert to a product having the analytical constants of cellulose triacetate.
7. It has been shown that in the saponification of cellulose acetate with aniline, at the boiling point of the aniline–cellulose acetate solution (*ca.* 183°) and at 148–151°, the acetyl–time curves present similar contours.

ROCHESTER, NEW YORK

---

[5] "Polarimetry," Bureau of Standards Circular 44, 2d ed., 1918, p. 81.

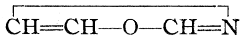
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

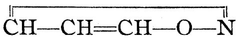
THE SYNTHESIS OF 4-(3,4-DIHYDROXYPHENYL)-THIAZOLES

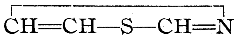
BY TREAT B. JOHNSON AND ELIZABETH GATEWOOD[1]

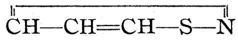
RECEIVED JANUARY 14, 1929 PUBLISHED JUNE 5, 1929

So far as the writers are aware, organic combinations derived from the heterocyclic rings—oxazole, I, isoxazole, II, thiazole, III, and isothiazole, IV, have never been utilized in the practice of general therapeutics, nor

I


II


III


IV


has their pharmacology been systematically investigated. This paper is the first of a proposed series from this Laboratory dealing with such cycles, and in which we shall describe methods of synthesizing new amino derivatives of the sulfur cycle, thiazole, represented by Formula III. All of the amines thus far prepared are being examined to determine their pharmacological action. The study of derivatives of the other three cycles included in the above heterocyclic series will be taken up as our investigation progresses.[2]

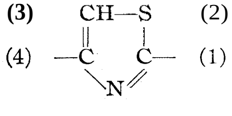
The basic idea which guided us in the formulation of our program of research was one of determining what influence the incorporation of a thiazole ring, III, or bridging with this cycle, would have on the potency and toxicity of known physiologically active organic substances. To illustrate, by the term "bridging" we mean the introduction of the compound radical—thyazyl,[3] C_3HNS— into the molecule of an amino acid like di-iodotyrosine, for example, leading to the formation of the unknown α-amino acid—*thyazyldi-iodotyrosine*—represented structurally by Formula V. In other words, this would lead to an analog of thyroxine, VI, which may also be viewed as a bridged compound derived from di-iodotyrosine, in which the compound radical, $I_2C_6H_2O$, functions in place of thyazyl in V. If we limit ourselves to thiazole substitutions in positions 2 and 4 of this cycle, only one other isomeric thyazyldi-iodotyrosine is theoretically possible, namely, that represented by Formula VII. The study of practical methods leading to the synthesis of these two acids, V and VII, is now in progress in this Laboratory.

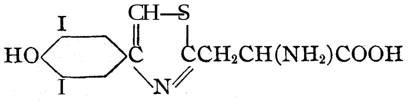
---

[1] Holder of the Metz Research Fellowship in Chemistry, 1926–1927.

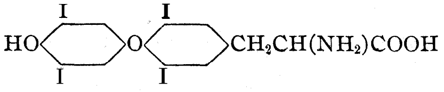
[2] Of the many possible constructions that may be derived from these four cycles, we are not interested, at present, in the different condensed ring systems of which henzovazoles and benzthiazoles, for example, are representative compounds.

[3] The thyazyl radical is represented structurally as



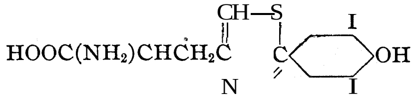


V

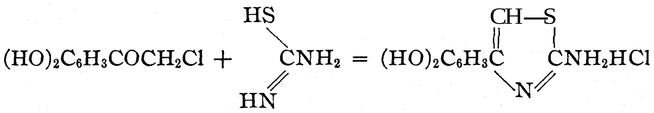


VI

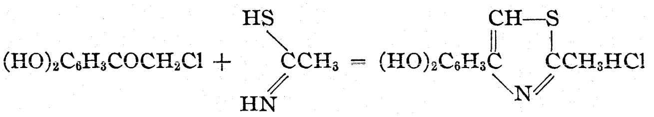
VII



In order to ascertain the influence of bridging with thyazyl, we first directed our attention to the study of methods of synthesizing thiazoles containing the catechol nucleus, $C_6H_3(OH)_2$. The catechol radical has been little used in drug synthesis except in the production synthetically of adrenaline and related compounds. The reaction which has led successfully to the synthesis of physiologically active thiazole derivatives is one based on the reactivity of an ω-chloroketone toward compounds containing thio-amide groupings. The mechanism of this reaction was first correctly interpreted by Hantzsch.[4] The only halogenated derivative of an aromatic ketone which has been extensively utilized in the development of thiazole chemistry is ω-chloro- or bromo-acetophenone, $C_6H_5COCH_2Br$. The halogenated ketone which served as the starting point of our research was chloro-acetocatechol, VIII, first described by Dzerzgowski,[5] and which served as the starting point for the first successful synthesis of adrenaline.[6] This chloro ketone interacts smoothly with every thio-amide construction that we have thus far examined, leading to the formation of thiazoles containing a catechol group in the 4-position of this cycle. The reactions with thiourea and acet-thioamnide, for example, are expressed below



VIII



In the Experimental Part of this paper is given a description of several new aminothiazoles containing the catechol group in the 4-position of the thiazole ring. An unexpected stability has been revealed in the case of the majority of the thiazole amines which we have thus far synthesized. Ordinarily, one expects to meet with organic constructions which easily undergo oxidation when experimenting with catechol derivatives. In our

---

[4] Hantzsch, *Ann.*, 249, 1 (1888); 250, 257 (1890); Traumann, *ibid.*, 249, 31 (1888).

[5] Dzerzgowski, J. Russ. *Phys.-Chem. Soc.*, 25, 154, 276 (1893).

[6] Stolz, Ber., **37**, 4149 (1904).

new compounds the bridging with the thiazole cycle has a decidedly stabilizing effect and our new catechol combinations can be preserved without undergoing rapid oxidation changes. Methods for synthesizing thiazole amines containing the cathechol group in the 2-position of this cycle will be described in our next paper.

Experimental Part

Chloro-acetocatechol, $ClCH_2COC_6H_3(OH)_2(3,4)$.—The chloro-acetocatechol used in the various condensation reactions described in this paper was prepared from catechol, chloro-acetic acid and phosphorus oxychloride both by the method of Mannich and Hahn,[7] without the use of a solvent, and the more recent method of Ott[8] in which the reaction is carried out in benzene.

The yields by the first method were improved by warming the mixture very gradually on a water-bath for several hours instead of heating at 100° for one hour and by using more phosphorus halide (1 mole). A sticky mass forms if the solution becomes too hot and the reaction mixture foams vigorously. We also applied Ott's procedure of synthesis but with slight modification in technique.

The following procedure gave the best results and the chloro-acetocatechol may usually be obtained very pure and in a colorless form by only one recrystallization.

Twenty grams of catechol, 20 g. of chloro-acetic acid and 15 g. of phosphorus oxychloride were dissolved in 80 cc. of benzene and the solution was warmed on a water-bath at about 60° for twenty-four hours. At the end of this time the solution was still light colored and contained a heavy deposit of crystalline chloro-acetocatechol. The solution was cooled, the benzene decanted and water then added. The precipitated ketone weighed 15 g. The benzene liquor usually gave a gram or two more when it was evaporated and the residue obtained was triturated with water. After one recrystallization from hot water the ketone melted sharply at 173°.

Preparation of **Acetamino-acetonitrile,** $CH_3CONHCH_2CN$.—Ten grams of the hydrochloride of amino-acetonitrile[9] was carefully warmed with 50 cc. of freshly distilled acetic anhydride until the solution became clear and effervesced vigorously. After allowing to stand for a few minutes the solution was diluted with benzene and then allowed to evaporate on a hot-plate. The residue solidified and after washing with ether weighed 10 g. The compound is purified by dissolving in chloroform and then precipitating by diluting the solution with ether. It melts at 77°.

Acetamino-acetothioamide, $CH_3CONHCH_2CSNH_2$.—A solution of 20 g. of acetamino-acetonitrile in 75 cc. of absolute alcohol and 25 cc. of concentrated aqueous ammonia was cooled to 10° and saturated with hydrogen sulfide. On allowing the solution to evaporate spontaneously, the thio-amide separated in a crystalline form and was purified by recrystallization from absolute alcohol. The yield was 19 g. and it melted at 123–124°.

Anal. Calcd. for $C_4H_8ON_2S$: N, 21.20. Found: N, 21.20, 21.05.

2-Acetaminomethyl-4-(3,4-dihydroxyphenyl)-thiazole. Hydrochloride.—Prepared by interaction of the above thioamide and chloro-acetocatechol in alcohol solution. It is easily purified by crystallization from alcohol and melts at 188–190°.

Anal. Calcd. for $C_{12}H_{13}O_3N_2SCl \cdot C_2H_5OH$: N, 8.08; C_2H_5OH, 13.28. Found: N, 7.72, 7.81; C_2H_5OH, 13.19.

---

[7] Mannich and Hahn, *Ber.*, 44, 1548 (1911).

[8] Ott, *ibid.*, 59, 1068 (1926).

[9] Curtius, *ibid.*, 31, 2490 (1898).

2-Aminomethyl-4-(3,4-dihydroxyphenyl)-thiazole, $(HO)_2C_6H_3\overline{C{=}CHSC(CH_2NH_2){=}N}$.—The hydrochloride of this thiazole base was obtained by digesting the above acetyl compound with concentrated hydrochloric acid. The salt was purified by dissolving in 85% alcohol and then precipitating by dilution with ether. It crystallized from hydrochloric acid in prisms melting at 225–230".

Anal. Calcd. for $C_{10}H_{10}O_2N_2S{\cdot}2HCI$: N, 9.49; Cl, 24.0. Found: N, 9.33; Cl, 24.3.

Acetylmethylamino-acetothio-amide, $CH_3CON(CH_3)CH_2CSNH_2$.—Twenty grams of methylamino-acetonitrile[10] was heated with 30 g. of acetic anhydride in benzene solution for thirty minutes. The solution was then evaporated to remove the solvent, the reaction product dissolved in cold saturated alcoholic ammonia, and the resulting solution saturated with hydrogen sulfide. We obtained 16 g. of thio-amide which crystallized from hot water in prismatic crystals melting at 156–157°. The compound is soluble in hot water or in alcohol and insoluble in ether.

Anal. Calcd. for $C_5H_{10}ON_2S$: N, 19.17. Found: N, 19.28, 19.21.

2-α-Acetamino-isopropyl-4-(3,4-dihydroxyphenyl)-thiazole, $(HO)_2C_6H_3\overline{C{=}CHSC(C(CH_3)_2NHCOCH_3){=}N}$.—a-Amino-isobutyronitrile was first prepared according to the method of Biltz and Slotta.[11] This was then acetylated[12] according to Hellsing's directions and from the acetyl compound was prepared the thio-amide by saturation in alcoholic ammonia solution with hydrogen sulfide. From 20 g. of the acetylated nitrile we obtained 14 g. of the thio-amide melting at 185–186°. Hellsing reports a melting point of 162°.

Five grams of this thio-amide and 5.6 g. of chloro-acetocatechol in 20 cc. of absolute alcohol were heated at the temperature of a boiling water-bath for thirty minutes. After cooling the hydrochloride of the thiazole was precipitated from this solution by dilution with ether. The yield was 8.0 g. It was purified by reprecipitation from alcohol and melted at 188–189°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2S{\cdot}HCl$: C, 51.1; H, 5.2; N, 8.5. Found: C, 51.2, H, 5.3; N, 8.3.

This salt is readily hydrolyzed by the action of cold water giving the free acetylthiazole. The latter was purified by crystallization from dilute alcohol. It separated in the form of prismatic crystals and melted at 198–200°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2S{\cdot}2H_2O$: N, 8.54; H_2O, 10.97. Found: N, 8.73, 8.51; H_2O, 10.78.

2-α-Amino-isopropyl-4-(3,4-dihydroxyphenyl)-thiazole, $(HO)_2C_6H_3\overline{C{=}CHSC(C(CH_3)_2NH_2){=}N}$.—Eight grams of the above hydrochloride of the acetylthiazole was digested with 50 cc. of strong hydrochloric acid for one hour. The hydrochloride of the aminothiazole began to separate from the solution almost immediately. We obtained 6 g. of the salt, which was purified by precipitating from alcohol solution with ether and recrystallization from hydrochloric acid. It melted with decomposition at 210–215°.

Anal, Calcd. for $C_{12}H_{14}O_2N_2S{\cdot}HCl{\cdot}H_2O$: N, 8.21; H_2O, 5.28. Found: N, 8.30, 8.50; H_2O, 5.17.

---

[10] Heimrod, *Ber.*, **47**, 347 (1914).

[11] Biltz and Slotta, *J. prakt. Chem.*, 113,241 (1926).

[12] Hellsing *Ber.*, **37**, 1924 (1904).

The thiazoles recorded in Table I were also prepared in the course of our research.

TABLE I

INCIDENTAL THIAZOLE COMPOUNDS

No.	Thiazole	Formula
1	2-Acetylmethylaminomethyl-4-(3,4-dihydroxyphenyl)-hydrochloride	$(HO)_2C_6H_3C{=}CHSC(CH_2N(CH_3)COCH_3){=}N \cdot HCl$
2	2-Methylaminomethyl-4-(3,4-dihydroxyphenyl)-	$(HO)_2C_6H_3C{=}CHSC(CH_2NHCH_3){=}N \cdot C_2H_5OH$
3	2-Mercapto-4-(3,4-dihydroxyphenyl)-	$(HO)_2C_6H_3C{=}CHSC(SH){=}N \cdot H_2O$[a]
4	2-Phenyl-4-(3,4-dihydroxyphenyl)-	$(HO)_2C_6H_3C{=}CHSC(C_6H_5){=}N$
5	2-Amino-4-(3'4-dihydroxyphenyl)-hydrochloride	$(HO)_2C_6H_3C{=}CHSC(NH_2){=}N$[b]
6	2-Methylamino-4-(3,4-dihydroxyphenyl)-hydrochloride	$(HO)_2C_6H_3C{=}CHSC(NHCH_3){=}N \cdot HCl$

[a] From ammonium dithiocarbamate and chloro-acetocatechol.

[b] From thiourea and chloro-acetocatechol.

No.	Formula	M. p., °C.	Nitrogen analyses Calcd., %	Pound, %	
1	$C_{13}H_{15}O_3N_2SCl$	186–188	8.90	8.85	9.11
2	$C_{11}H_{12}O_2N_2S \cdot C_2H_5OH$	128–130[a]	9.93	9.92	10.01
3	$C_9H_7O_2NS_2 \cdot H_2O$[b]	250	5.76	5.76	5.72
4	$C_{15}H_{11}O_2NS$	164–165	4.86	4.56	4.69
5	$C_9H_9N_2SCl \cdot H_2O$[c]	230–235	10.7	10.6	
6	$C_{10}H_{11}O_2N_2SCl$[d]	275–280	10.8	10.5	

[a] Hydrochloride m. p., 220–225". [b] H_2O, calcd.: 7.41. Pound: 7.37. [c] Calcd.: C, 41.1; H, 4.2. Found: C, 41.6; H, 4.3. [d] Calcd.: C, 46.4; H, 4.3. Found: C, 46.8; H, 4.3.

Summary

1. The halogenated ketone ω-chloro-acetocatechol, $ClCH_2COC_6H_3(OH)_2$, has been shown to interact smoothly with organic compounds containing thio-amide groupings.

2. These condensations lead to the formation of new thiazoles containing the catechol group in position 4 of the thiazole cycle.

3. In this paper we have given methods for preparing several new aminothiazoles. All of these compounds thus far examined have been found to be physiologically active.

4. They are characterized by their stability in the air, notwithstanding the presence of a catechol grouping in their respective molecules.

5. This research on thiazoles is being continued in this Laboratory. It will include a study of the pharmacology of our new synthetic compounds.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CARBOHYDRATE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

OPTICAL ROTATION AND ATOMIC DIMENSION. VIII. HALOGENO-HEPTA-ACETYL DERIVATIVES OF MELIBIOSE AND MALTOSE. THE STRUCTURES OF BIOSES AND CELLULOSE

BY D. H. BRAUNS

RECEIVED JANUARY 14, 1929 PUBLISHED JUNE 5, 1929

In preceding articles of this series it was reported that the relation between the specific rotational values and the atomic dimensions of the halogeno-hepta-acetyl derivatives of cellobiose, glucosido-mannose and gentiobiose deviate from the regular relationship for the monose sugars and that an agreement is obtained only by excluding the values for the fluoro derivatives. In this relationship these three bioses behave in the same manner, although their structure is not alike. In celloboise and glucosido-mannose the first carbon of the one monose is connected by an oxygen atom to the *fourth* carbon of the second, whereas in gentiobiose the first carbon of the one monose is connected by an oxygen atom to the *sixth* carbon of the other.

The preparation and rotational values of the pure crystalline fluoro-, chloro- and bromo-hepta-acetyl derivatives[1] of melibiose, which are described in the present article, have revealed the astonishing fact *that an exact agreement with the regular relationship for the monose sugars exists for these biose derivatives.* The recent establishment of the structure of melibiose[2] has shown that in this biose the first carbon of the one monose, galactose, is attached by an oxygen atom to the sixth carbon atom of the other, glucose, and, further, that melibiose is an *α-biose.*[3] Melibiose is therefore a-galactosido-6-glucose. *The bioses which have been investigated before,* cellobiose, glucosido-mannose and gentiobiose, are *β-bioses.*

Before making deductions from this striking difference in behavior of these a-and β-bioses, it seemed desirable to check this result. This pointed directly to the necessity of preparing the halogen derivatives of maltose, as it has been established that maltose[4] is a-glucosido-4-glucose and it was considered probable that an a-6-biose and an a-4-biose would behave in the same way. In addition to the melibiose derivatives this paper describes

---

[1] The crystalline iodo derivative was too unstable to allow a process of recrystallization. The rotational value of the yellowish crystals was found to be close to the value required by the atomic dimension relationship.

[2] Haworth, and co-workers, *J. Chem. Soc.,* 1527, 3146 (1927); Helferich and Bredereck, ***Ann.,*** 465,166 (1928).

[3] Bioses in which the reducing or first carbon atom of the one monose is connected by an α-glucosidic bond to one of the non-reducing carbons of the second monose are called a-bioses. The reducing (first) carbon of the second monose allows the substitution of its hydroxyl for halogen.

[4] Haworth, Loach and Long, *J.* Chem. *Soc.,* 3146 (1927).

the preparation of pure crystalline fluoro- and bromo-hepta-acetylmaltose[5] and gives their rotational values. The rotational value for the crystalline chloro derivative has been checked with that reported in the literature. The iodo derivative could not be obtained in crystalline condition. The data for the specific rotations of the melibiose and maltose derivatives together with those for the other bioses are given in Table I for comparison with the regular relationship of the monose sugars.

TABLE I

COMPARISON OF SPECIFIC ROTATIONS OF α- AND β-BIOSE DERIVATIVES[a] WITH REPRESENTATIVE MONOSE DERIVATIVES (INCLUDING FLUORO DERIVATIVES)

	a-Bioses Deriv. of		β-Bioses Deriv. of			Resp. sp. rot. diff.					Resp. sp. rot. diff. reduced					Sp. rot. diff., monoses
	Melibiose	Maltose	Gentiobiose	Cellobiose	Glucomannose	a		β			α		β			
F	149.7	111.1	43.8	30.6	13.6											
						42.8	48.4	36.7	41.1	37.6	41	41	41	41	41	41
Cl	192.5	159.5	80.5	71.7	51.2											
						17.4	20.6	20.6	24.1	26.7	17	17	23	24	29	17
Br	209.9	180.1	101.1	95.8	77.9											
						..	..	25.0	29.9	33.6	..	..	28	30	37	21
I	..	..	126.1	125.7	111.5											

[a] All rotations recorded in Tables I and II are positive.

TABLE II

COMPARISON OF SPECIFIC ROTATIONS OF β-BIOSE DERIVATIVES WITH REPRESENTATIVE MONOSE DERIVATIVES (EXCLUDING FLUORO DERIVATIVES)

	β-Bioses Derivatives of Gentiobiose	Cellobiose	Glucomannose	Resp. sp. rot. diff.			Resp. sp. rot. diff. reduced			Sp. rot. diff., monoses
Cl	80.5	71.7	51.2							
				20.6	24.1	26.7	17	17	17	17
Br	101.1	95.8	77.9							
				25.0	29.9	33.6	21	21	21	21
I	126.1	125.7	111.5							

The foregoing data adequately support the conclusion that the a-biose derivatives follow the atomic dimension relationship, whereas the β-biose derivatives agree with this relationship only when the fluorine derivatives are excluded.

Directed by the atomic dimension relationship, I thus concluded that *a* fundamental difference between the finer structures of these a- and β-bioses must exist, as the numerical deviation of the atomic dimension relationship for each of the β-bioses must be an expression of this difference in structure.

---

[5] The preparation of pure crystalline bromo-hepta-acetylmaltose, which has been intermittently attempted by the author during many years, has revealed peculiarities which may be of interest from a chemical and crystallographical standpoint. The results are given under "Experimental Part."

Discussion of Results

Two postulates have been used for arriving at an insight into the finer structure of the bioses. The first postulate is the basis of stereo-chemistry of carbon compounds. The second postulate is based on the present view of the stereo-chemical behavior of oxygen.

Postulate I.—The directions of the four equal valences of the carbon atom are the same as the directions of the lines connecting the four corners of the regular tetrahedron with its center.

Postulate 11.—Two possibilities exist for the oxygen atom: *(a)* The directions of the four valences (two primary and two secondary) of oxygen are the same as those for the valences of the carbon atom. The oxygen atom displays valences of this kind in the ring system of the monoses. (b) The two primary valence directions of oxygen are nearly opposite each other. (In the present discussion it is assumed that valences of these types are displayed by the oxygen atom which connects the two monoses of *a*- and of β-bioses.)

For support of the second postulate I quote Huggins,[6] who states that "for one reason or another a valence may be forced away from its normal position. Thus in the quartz crystal the angle subtended at the atomic center by the two bond electron pairs around each oxygen atom is considerably greater than it would be if the pairs were in their normal positions at the corners of a regular tetrahedron (about 109°)."

Allowing these postulates, let us consider first one carbon atom to which four different single atoms are attached and call the first valence the α-valence and the second the p-valence. These ***a***- and β-valences are symmetrically arranged with respect to the plane going through the other two valences, in which plane the centers of the carbon atom and the third and the fourth atoms are also situated. The *a*- as well as the β-valence makes with this plane an angle of $109.5^\circ/2 = 54.75^\circ$, whereas the a-valence makes with the p-valence an angle of 109.5".

This regularity does not hold, however, for a ring system, as, for example, the amylene-oxide structure of the monose sugars. Using the facts laid down in the written formula of glucose, we will systematically build up in space the structure formula for this sugar and in this way bring out some peculiar differences in structure between the *a*- and β-forms of the monoses.[7]

Suppose we first make a row of the six carbons of glucose. The valence

---

[6] Huggins, Phys. ***Rev.***, **19,352** (1922).

[7] Dowel pins and wooden cubes with 26 holes (Bool Furniture Co , Ithaca, N. Y.) are recommended for making models. The rigid angles and the close connection of the blocks prevent the errors that are easily made when wire is used for the bonds. Tetrahedrons are easily constructed from the cubes. Oxygen is indicated by a black triangle on each face.

connecting the first with the second carbon is directed at a definite angle *upward* (with regard to a horizontal plane), whereas the valence connecting the second to the third carbon must necessarily be directed the *same angle downward,* and so on. The centers of these six carbons are thus situated in two horizontal lines, one above the other, the first, third and fifth in the lower and the second, fourth and sixth in the higher. We will call this the zig-zag chain of six carbons. The attaching of the hydroxyl groups to the carbons is not *directly* given by the conventional glucose formula of Fischer–Tollens–Haworth, because it must be realized which agreement had to be made in order that space relations could be expressed in a *plane* (of the paper). It follows from these agreements that if the model of the zig-zag chain of carbons is placed on a horizontal plane and viewed from above, *each* carbon must be viewed in succession and from such a side that the extension of the valences connecting this carbon to the former and to the next are *crossing this plane.* Therefore, if the second carbon in the zig-zag chain is situated in a horizontal plane *above* that of the first carbon, we can directly put the OH group at the right without being obliged to turn the model.[8] For the OH group of the third carbon, however, which should have a left position according to the written formula, we have to turn the zig-zag model around in order to view this carbon from the correct side (in which the extension of the valences connecting this carbon to the former and the next are crossing the horizontal plane on which the model is placed). Consequently the OH of the third carbon comes in the zig-zag chain model at the *same side* as the OH of the second carbon. The OH of the fourth carbon will come in the zig-zag model also under the OH of the preceding carbons, whereas the OH of the fifth carbon (represented by an oxygen block) will be situated at the *other* side of the zig-zag model, as will be easily seen by consulting the written formula for glucose.

In order to make the amylene-oxide ring we leave the connection between the first carbon and the second as it is, and turn the third carbon around the **2–3** axis until its OH group is opposite that of the second. Now we turn the fourth carbon around the **3-4** axis until its OH is opposite that of the third. At last the fifth carbon is turned around the 4–5 axis until its oxygen (represented by an oxygen block) closes the six-numbered ring by also turning the first carbon around the 1–2 axis.

The ring is formed without strain and the model has much regularity. If viewed from the side of the ring a perfect representation of Fischer's written glucose formula is given, the agreements being taken into account. The place of the sixth carbon, however, which is below the plane of the

---

[8] It is convenient to indicate the OH groups of the second, third and fourth carbons by dowel pins and omit the indication of the H atoms. However, the OH group of the fifth carbon is indicated by a block representing oxygen.

ring and which assumed this position by the turning of the 4–5 axis, could not be so easily found without the preceding logical deduction.[9]

I will give now a brief description of the finished model, bringing out peculiarities for the direction of the a- and β-valences. If the model is so placed that the ring is horizontal and the first carbon be situated farthest away from the observer with the second carbon at the left and the oxygen atom at the right, then the valence connecting the first carbon to the second is directed at a definite angle upward and that from the second to the third at the same angle downward, and so on. Consequently the centers of the first, third and fifth carbons will be in one horizontal plane, and those of the second and fourth carbons and the oxygen will be in a second horizontal plane slightly above the first. The unoccupied valences of the first carbon are always designated as a- and β-valence. It has been established that the a-valence for all-d-sugars must be at the top of this carbon in accord with the requirement[10] that for d-glucose it must be near the OH group of the second carbon which is at the top of the second carbon. Now we observe that *the a-valence is directed slightly upward to the front, making an angle with the horizontal ring system of about 19.5°, whereas the β-valence is directed about perpendicularly down, making therefore an angle of about 90° with that ring system.*[11] This result is entirely different from that obtained for a single carbon atom, to which four different atoms are attached and for which the α- and β-valences are *symmetrically* placed with regard to the plane in which the third and fourth atoms are situated. The explanation of this peculiarity for the monoses is that the directions of the a- and β-valences are not *primarily* dependent on the direction of the parallel planes of the ring systems, *but on the direction of the valence connecting the first carbon to the second* (or the first to the sixth).

Before we show how the experimental facts regarding the rotational relationship of the halogeno-acetyl derivatives of the bioses are well explained by structural peculiarities of the bioses, it seems well to point out plainly the two *assumptions* on which these *finer* stereo-chemical structures are based.

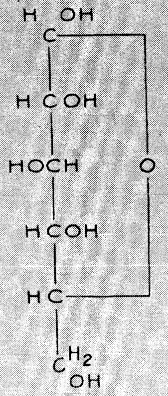
I. The particular ring structure of the monoses developed above is

---

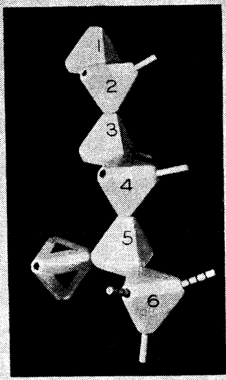
[9] I am indebted to Prof. W. H. Dore of Berkeley (California) for valuable remarks establishing this place of the sixth carbon atom.

[10] Boeseken, Ber., 46,2612 (1913); Pictet, Helv. *Chim. Acta,* 3,649 (1920); Hudson, THIS JOURNAL, 31, 66 (1909). For the I-sugars the @-valence is that of the top as required by the nomenclature.

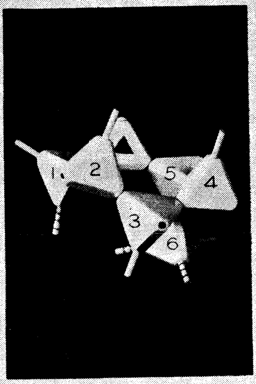
[11] The difference in direction of the α-valence and the @-valence with respect to the ring system has been logically derived from the tetrahedral orientation of the four valences of the carbon atom. The anisotropy of the carbon atom [see the interesting study on this subject by Mrs. K. Lonsdale-Yardley, *Phil.* Mag., 6, 433 (1928)] may also have a *minor* influence on this different behavior of the α- and @-valences.



WRITTEN FORMULA

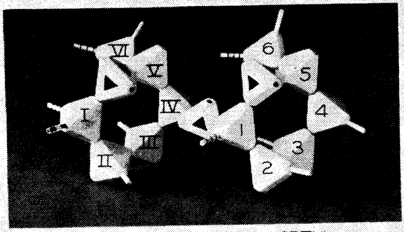


ZIG-ZAG FORMULA
ALDEHYDE GROUP OMITTED

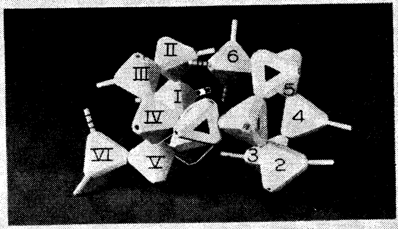


STEREO FORMULA

α-GLUCOSE

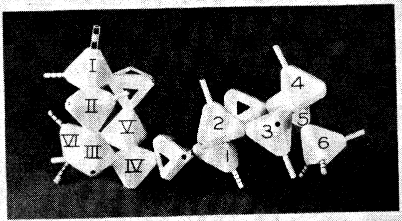


HALOGENO-HEPTA-ACETYL
CELLOBIOSE
NON-FACING FORMULA

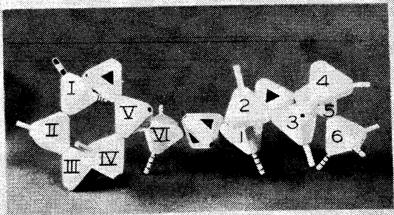


HALOGENO-HEPTA-ACETYL
CELLOBIOSE
FACING FORMULA

β-BIOSE DERIVATIVES



HALOGENO-HEPTA-ACETYL
MALTOSE



HALOGENO-HEPTA-ACETYL
MELIBIOSE

α-BIOSE DERIVATIVES

△ CARBON ATOM
▲ OXYGEN ATOM
▭ HYDROXYL OR ACETYL GROUPS
▬ HALOGEN (ALWAYS IN α-POSITION)
┅ HYDROGEN ATTACHED TO THE FIRST AND SIXTH CARBON, ALL OTHERS OMITTED.

THE CARBON ATOMS OF THE HALOGEN CONTAINING MONOSE ARE NUMBERED BY ROMAN FIGURES; THE CARBON ATOMS OF THE OTHER MONOSE BY ARABIC FIGURES.

only one of the several possible spacial arrangements of the atoms in the amylene oxide ring.[12]

II. It is assumed that the linking oxygen between the monose units has its valences opposite each other and that a free rotation of the monose units around this oxygen linkage can take place.

Important deductions can now be made regarding the structure of α- and β-bioses, which were studied in the forms of their halogen derivatives. We will apply a free rotation around the axis which connects the one monose by an a-(or β-) valence by means of an oxygen atom to the second monose for the *a*- and β-bioses, respectively. Taking into account the small angle (19°) which the a-valence makes with the ring system, it can be seen even without a model that for the a-bioses (melibiose and maltose) the halogen atom is too far away from the other monose to be influenced by secondary valences. We can turn the second monose entirely 360° around the connecting a-valence axis without an appreciable approach of the ring systems. With the investigated β-bioses, however, it is quite different. We will first connect the two ring systems through the β-valence and an oxygen atom to the fourth carbon (cellobiose and glucosido-mannose) in such a way that the second ring is situated in *front* of the other in a parallel horizontal plane below the first. When the second monose is turned from 90 to 180° around the β-biosidic axis, it is seen *that the halogen attached to the a-valence of the second monose faces the atoms attached to the ring system of the first monose. The same result* is obtained by connecting the two ring systems through the β-valence and an oxygen atom to the sixth carbon (gentiobiose). These model studies, directed by experimental results, clearly explain *that the halogens of the β-bioses are influenced by secondary valences, whereas the halogens of the α-bioses are not.* Further, these model studies indicate that some β-bioside derivatives, as β-glucosido-4-galactose, must follow entirely the atomic dimension relationship. Investigations will be taken up later for checking this result and also for determining more exactly which are the selectively influencing atoms of the second monose.

This insight into the finer structure of the bioses, resulting from the application of the atomic dimension relationship, gives also a suggestion regarding the structure of such important polysaccharides as *cellulose.* The old formula for cellobiose cannot be used for constructing the formula for cellulose, as the x-ray picture of cellulose fiber shows a diffraction pattern requiring C_{12} units, whereas the above old formula of cellobiose in chain formation would require a pattern of C_6 units.[13]

---

[12] See, e. *g.,* Lowry, *Chem. Industry,* 47, 1149 (1928).

[13] See Sponsler and Dore, "Colloid Symposium Monograph," Chemical Catalog Co., New York, p. 174, and THIS JOURNAL, 50, 1941 (1928); also, Hauser, *Ind. Eng. Chem., 21, 120* (1929). Nor does a ring formula of three units, for example, satisfy the requirements on account of the low molecular weight and weak secondary bonds of

However, the new structure formula for cellobiose in chain formation, in which one glucose of the cellobiose molecule is facing the other, *fulfils* the pattern *requiring* C_{12} *units,* although at this stage of the investigations it would also allow larger units such as C_{18}. An examination of a model of this chain of C_{12} units shows further that the oxygen atoms connecting the successive glucose units are alternately well protected and partly protected by surrounding groups[14] (especially by acetyl groups of the first and second carbon atoms), which fact explains why *cellobiose* is produced on acetolysis of *cellulose fiber,* as the one oxygen union will be hydrolyzed more quickly than the next.

These peculiarities, revealed by a study of the atomic dimension relationship, lead to a conclusion regarding the possibility of considering cellobiose as a building stone of cellulose opposite that heretofore adopted. We now see that the former conclusion was erroneous because a formula for cellobiose had been adopted for which sufficient detail in structure was lacking.

Experimental Part

General Remarks.—For all determinations of the specific rotation U. S. P. or purified chloroform[15] was used. The volume of the solution was made up in the same flask to 24.9767 cc. at 20°, which requires multiplication by the factor 4.0038 for obtaining 100 cc. The reading, which was made in the same 4-dm. tube at 20°, is given in circular degrees.

Melibiose.—A supply of β-melibiose dihydrate was prepared from raffinose according to the method of Hudson and Harding.[16] After one recrystallization the preparation gave a specific rotation in water of +128.9°, agreeing with the value obtained by Hudson and Yanovsky[17] of +129.5°.

β-Octa-acetylmelibiose was prepared by acetylating melibiose with acetic anhydride and anhydrous sodium acetate. It was recrystallized four times from 95% alcohol, yielding a product of constant specific rotation in chloroform of +102.6° and m. p. 177". Hudson and Johnson[18] report specific rotation in chloroform +102.5°; m. p. 177.5" (corr.).

Fluoro-hepta-acetylmelibiose was prepared from β-octa-acetylmelibiose in the manner previously described.[19] The distillation was finished in about twenty to twenty-five minutes and the reaction product was directly worked up. The sirup resulting from the extraction with chloroform did not crystallize readily. Crystallization was

---

the chain in contradiction to the tensile strength [Meyer and Mark, *Ber.*, 61,593 (1928); Hess and Trogus, *ibid.*, 61, 1982 (1928)].

[14] Acetyl or acyl groups are, of course, not extending from a carbon atom of the ring system in a straight line connecting the corner of the tetrahedron with its center, but are curved out from the ring system by the O—CO—C bond. As to the 50% yield of cellobiose octa-acetate from cellulose, see Friese and Hess, *Ann.*, **456,** 42 (1927).

[15] Brauns, THIS JOURNAL, 46, 1486 (1924).

[16] Hudson and Harding, *ibid.*, 37,2734 (1915).

[17] Hudson and Yanovsky, *ibid.*, 39, 1027 (1917)

[18] Hudson and Johnson, *ibid.*, 37,2752 (1915).

[19] Brauns, *ibid.*, 45,834 (1923).

started by adding some 70% methyl alcohol and scratching the walls of the dish. When crystallization started more 70% methyl alcohol was added gradually. The yield of impure crystals was 8 g. from 15 g. of β-octa-acetate. It was recrystallized several times by being dissolved in boiling 70% methyl alcohol with addition of decolorizing carbon and filtered through an ordinary folded filter. The filtrate was seeded and allowed to cool gradually. The first separations of the recrystallizations of the impure substance contain most of the impurities. The pure product crystallizes in small prismatic needles and is stable, colorless and tasteless. It is very soluble in most solvents except water and petroleum ether; m. p. 135°. The determination of the specific rotation in chloroform solution gave the following result.

Rotation.—Third recrystallization; first and second fractions, respectively. Subs., 0 5247, 0.6429: a = +12.445°, +15 374°; $[\alpha]^{20}_{D}$ = +148 12°, +149.31°. Fourth recrystallization: first and second fractions, respectively. Subs., 0.6225, 0.3722: α = +14.923°, +8.900°; $[\alpha]^{20}_{D}$ = +149.69°, +149.36". Fifth recrystallization: first and second fractions, respectively. Subs., 0 6412, 0 2132: a = +15.374°, +5.098°; $[\alpha]^{20}_{D}$ = +149.71°, +149.31°. Therefore \$149.70" is taken as the specific rotation of the pure substance.

Anal. Subs., 0.1679: CO_2, 0.2999; H_2O, 0.0847. Subs., 0.5000: CaF_2, 0.0269. Subs., 0.5000: 98.54 cc. of 0.25 *N* H_2SO_4, 246.35 cc. of 0.1 N NaOH. Calcd. for $C_{26}H_{35}O_{17}F$: C, 48.88; H, 5.53; F, 2.98; 62.67 cc. of 0.1 N NaOH for AcOH + F. Found: C, 48.71; H, 5.64; F, 2.62; 61.95 cc. of 0.1 *N* NaOH.

Chloro-hepta-acetylmelibiose was prepared by following the method described for chloro-hepta-acetylgentiobiose.[20] The sirup resulting from the concentration of the chloroform solution did not crystallize readily, a difficulty which was observed for all the halogen derivatives of melibiose. The following method was employed for obtaining the chloro derivatives in a crystalline condition. The sirup was kept first for a few hours in a vacuum desiccator. A small quantity of ether mixed with about one-fourth of its volume of petroleum ether was then added and the mixture was continually stirred while the sides of the crystallizing dish were scratched; the solid masses separating at the walls of the dish were broken down. Gradually a cloudiness appeared. A small quantity of ether was then added and the stirring was continued until small crystals separated. At this stage more ether was added, accelerating the crystallization. The crystals were separated on a suction filter. The yield of impure crystals was 6 g. from 20 g. of β-octa-acetate. A small quantity of crystals was always put aside for seeding the solution of the next recrystallization. Recrystallization was produced by dissolving in dry ether, filtering and slowly evaporating the solution under a bell jar with a current of dry air. The concentrated solution was seeded and the slow evaporation continued. The current of air was interrupted after fifteen minutes and the solution was allowed to stand undisturbed for ten to twenty minutes. In this way well developed crystals were obtained. The determination of the specific rotation in chloroform gave the following results.

Rotation.—Second recrystallization: first and second fractions, respectively. Subs., 0.6626, 0.6261: a = +20.416°, +19.238°; $[\alpha]^{20}_{D}$ = +192.39°, +191.86°. Third recrystallization: first and second fractions, respectively. Subs , 0.6327, 0.6299: a = +19.498°, +19.422°; $[\alpha]^{20}_{D}$ = +192.42°, +192.52°.

Therefore, 192.50" is taken as the specific rotation of the pure substance. The pure compound crystallizes in small prisms; m. p. 127". It is slightly bitter and stable when kept in a vacuum desiccator over sodium hydroxide in the ice box. It is readily soluble in ordinary solvents except petroleum ether and water, and slightly soluble in ether.

---

[20] Brauns, THIS JOURNAL, 49,3173 (1927).

Anal. Subs, 0 2019: CO_2, 0.3504; H_2O, 0.0990. Subs., 0.2315: AgCl, 0.0514. Subs., 0.5000: 98.54 cc. of 0.25 *N* H_2SO_4, 306.95 cc. of 0.1 NaOH. Calcd. for $C_{26}H_{35}O_{17}Cl$: C, 47.65; H, 5.39; Cl, 5.41; 61.10 cc. of 0.1 *N* NaOH. Found: C, 47.33; H, 5.48; Cl, 5.49; 60.60 cc. of 0.1 *N* NaOH.

Bromo-hepta-acetylmelibiose.—Twenty-five grams of octa-acetylmelibiose was dissolved in 85 cc. of acetic acid and 62 cc. of a saturated solution of hydrogen bromide in acetic acid was added. The mixture was kept in a stoppered Erlenmeyer flask at room temperature for one and one-half hours. It was then poured into a separatory funnel containing ice water, cracked ice and chloroform and shaken out five times with ice water. The chloroform extract was dried with calcium chloride, filtered and evaporated to a sirup at low temperature. The sirup was stirred with 15 cc. of petroleum ether and the petroleum ether solution was poured off. This process was repeated once. The petroleum ether solution crystallized overnight by evaporation in the air. The quantity of crystals was small but it was useful for seeding the ether solution of the sirup. The process for obtaining well-defined pure crystals was the same as that described for chloro-hepta-acetylmelibiose. The yield was small, being 4 g. from 25 g. of octa-acetate. The solutions for the rotations were prepared with purified chloroform.

Rotation.—First recrystallization. Subs., 0.6184: a = +20.642°; $[\alpha]^{20}_{D}$ = +208.-42". Second recrystallization. Subs., 0.6127: a = +20.538°; $[\alpha]^{20}_{D}$ = $209.30". Third recrystallization. Subs., 0.6336: α = +21.297°; $[\alpha]^{20}_{D}$ = +209.88°. Fourth recrystallization. Subs., 0.4256: a = +14.293°; $[\alpha]^{20}_{D}$ = +209.70°.

Therefore, +209.90° is taken as the specific rotation of the pure substance. The pure substance crystallizes in short prisms; m. p. 116". It is slightly bitter and can be kept in a vacuum desiccator over sodium hydroxide in the ice box. It is readily soluble in most solvents, less soluble in ether and slightly soluble in petroleum ether and water.

Anal. Subs., 0 2360: CO_2, 0.3842; H_2O, 0.1090. Subs., 0.1960: AgBr, 0.0529. Subs, 0.5000: 98.54 cc. of 0.25 N H_2SO_4, 303.46 cc. of 0.1 *N* NaOH. Calcd. for $C_{26}H_{35}O_{17}Br$: C, 44.62; H, 5.05; Br, 11.43; 57.20 cc. of 0.1 NNaOH. Found: C, 44.40; H, 5.17; Br, 11.48; 57.11 cc. of 0.1 NNaOH.

β-Octa-acetylmaltose was prepared by acetylating maltose with anhydrous sodium acetate and acetic anhydride. It was recrystallized twice from 95% alcohol, yielding in chloroform a product of constant specific rotation +62.87° and m. p. 159–160°. Hudson and Johnson[Z1] report $[\alpha]^{20}_{D}$ = +62.59° and m. p. 159–160°.

Fluoro-hepta-acetylmaltose.—Ten grams of β-octa-acetylmaltose was treated with anhydrous hydrofluoric acid in the manner previously described.[17] The distillation was finished in about twenty to twenty-five minutes and the reaction product was worked up directly. The sirup resulting from the extraction with chloroform was crystallized by stirring with petroleum ether, the yield of impure crystals being 7.5 g. from 10 g. of octa-acetate. It was recrystallized several times by dissolving in about 80 cc. hot 95% alcohol, filtering and cooling gradually, at last with ice. The pure product crystallizes in small prisms and is stable, colorless and tasteless. It is soluble in the ordinary solvents except petroleum ether and water; m. p. 174–175°. The determination of the specific rotation in chloroform gave the following results.

Rotation.—First recrystallization. Subs., 0.7097: α = +12.574°; $[\alpha]^{20}_{D}$ = +110.-62°. Second recrystallization. Subs., 0.7208: a = +12.806°; $[\alpha]^{20}_{D}$ = +110.93°. Third recrystallization. Subs., 0.7143: α = +12 709°; $[\alpha]^{20}_{D}$ = +111.10°. Fourth recrystallization. Subs., 0.6975: α = +12.411°; $[\alpha]^{20}_{D}$ = +111.10". Therefore, +111.1° is taken as the specific rotation of the pure substance.

Anal. Subs, 0.2066: CO_2, 0.3717; H_2O, 0.1062. Subs., 0.5067; CaF_2, 0 0251.

---

[21] Hudson and Johnson, THIS JOURNAL, 37,1276 (1915).

Subs., 0.5000: 106.18 cc. of 0.25 *N* H_2SO_4, 328.35 cc. of 0.1 N NaOH. Calcd. for $C_{26}H_{35}O_{17}F$: C, 48.88; H, 5.53; F, 2.97; 62.67 cc. of *N* NaOH. Found: C, 49.06; H, 5.75; F, 2.41; 62.90 cc. of 0.1 *N* NaOH.

Chloro-hepta-acetylmaltose has been obtained in crystalline condition by Foerg[22] by saturating an acetic anhydride suspension of maltose with hydrochloric acid at low temperature. The container was sealed and kept for two weeks at room temperature. Foerg separated from the reaction product crystalline chloro-hepta-acetylmaltose, but made an error in recording the sign of the specific rotation, which was corrected by Schliephacke,[23] who found for the specific rotation in chloroform solution +158.68°. By applying the chlorination method of von Arlt, modified by Skraup and Kremann,[24] described for the preparation of chloro-tetra-acetylmannose,[25] I prepared pure chloro-hepta-acetylmaltose in a few days.

The reaction product, a colorless sirup, crystallized when stirred with petroleum ether. The yield of impure crystals was 9 g. from 15 g. of β-octa-acetate. Recrystallization was produced by dissolving in warm ether, filtering and adding so much petroleum ether that seeding or scratching started the crystallization. Recrystallization was repeated until a constant-rotating substance was obtained. The pure product crystallizes in small prisms and is stable when kept in a desiccator over sodium hydroxide in the ice box. It is soluble in the ordinary solvents except petroleum ether and water; m. p. 125". Foerg and Schliephacke report m. p. 118–120°. The determination of the specific rotation in chloroform gave the following results.

Rotation.—First recrystallization. Subs., 0.6044: $a = +15.370°$; $[\alpha]_D^{20} = +158.79°$. Second recrystallization. Subs., 0.6471: $a = +16.504°$; $[\alpha]_D^{20} = +159.25°$. Third recrystallization. Subs., 0.6484: $\alpha = +16.549°$; $[\alpha]_D^{20} = +159.36°$. Fourth recrystallization. Subs., 0.6145: $a = +15.693°$; $[\alpha]_D^{20} = +159.46°$. Therefore +159.50° is taken as the specific rotation of the pure substance.

Anal. Subs., 0.1878: CO_2, 0.3263; H_2O, 0.0899. Subs., 0.2733: AgCl, 0.0605. Calcd. for $C_{26}H_{35}O_{17}Cl$: C, 47.65; H, 5.39; Cl, 5.41. Found: C, 47.39; H, 5.36; Cl, 5.47.

Bromo-hepta-acetylmaltose.—Crystalline bromo-hepta-acetylmaltose has been described by Fischer and Armstrong[26] in a short communication. They obtained it by the action of liquid hydrobromic acid on octa-acetylmaltose under high pressure at room temperature, evaporating the hydrobromic acid and crystallizing the reaction product from hot ligroin. Prismatic needles were obtained melting at 84°. A bromine determination gave correct figures for a monobromo derivative, but no other properties were recorded. In a later paper Fischer[27] stated that by repeating this method of preparation an amorphous product resulted, which was largely the monobromo derivative, as a high percentage of crystalline hepta-acetyl-

---

[22] Foerg, Monatsh., 23, 45 (1902).

[23] Schliephacke, Ann., 377, 184 (1910).

[24] Von Arlt, Monatsh., 22, 144 (1901); Skraup and Kremann, ibid., 22, 376 (1901).

[25] Brauns, THIS JOURNAL, 44, 404 (1922).

[26] Fischer and Armstrong, *Ber.*, 35, 3153 (1902).

[27] Fischer, ibid., 44, 1898 (1911); also E. Fischer and H. Fischer, ibid., 43, 2522 (1910).

maltose could be obtained from it. Later investigators have always used this amorphous product, for example, Karrer.[28] In the course of the present investigation the following facts were brought out which are important for preparing the crystalline bromo derivative.

1. The use of liquid hydrobromic acid, which requires the cooling with liquid air, yields a crude product which does not differ from the crude products of more simple methods of preparation.

2. It is advantageous to prevent so far as possible the formation of the dibromo derivative (which is not easily separated from the monobromo derivative) by shortening the time of reaction.

3. The crude amorphous product crystallizes from hot ligroin only if the cooling or concentrating is extremely slow. This slow cooling was produced by the use of unsilvered Dewar flasks and slow evaporation by a very weak current of dry air.

Preparation.—Five grams of octa-acetylmaltose was dissolved in 17 cc. of acetic acid which had been cooled to about 15°. Then 11 cc. of a saturated solution of hydrogen bromide in acetic acid was added and the whole was cooled to about 0°. The mixture was kept in a stoppered Erlenmeyer flask in ice water for half an hour and was then poured into a separatory funnel containing ice water and cracked ice and shaken out five times with ice water, yielding a neutral chloroform solution. This was dried with calcium chloride, filtered and evaporated to a sirup at low temperature by a current of dry air. The sirup was allowed to stand in a vacuum desiccator for two hours, after which it was converted to a sticky white powder by stirring with ligroin (b. p. 70–90°). This powder was boiled on the steam-bath in an Erlenmeyer flask with about 100 cc. of ligroin for some five minutes, forming a sticky substance which was stirred with a glass rod. The hot solution was then poured without filtering into an unsilvered Dewar flask, the sticky sediment remaining in the Erlenmeyer flask. This process was repeated. The wall of the Dewar flask was then scratched with a glass rod, which was first rubbed in some crystalline bromo derivative (obtained by repeatedly pouring off a ligroin solution from amorphous separations). After standing overnight crystalline material separated at the walls and amorphous substance at the bottom of the Dewar flask. The mother liquor was poured into beakers and very slowly evaporated under a bell jar by a weak current of air. By seeding and scratching the walls of the beakers brilliant short prisms of about one mm. in thickness and length were obtained. The amorphous product, which separates at the bottom of the Dewar flasks, can be converted to crystals by repeating the foregoing process. The analysis of the amorphous substance yields figures which are near those required for the monobromo derivative and its specific rotation is only a few degrees lower than that for the pure crystalline compound. Its melting point, however, is different as it melts at 80–83°. Heated quickly to near its melting point it was found that crystalline bromo-hepta-acetylmaltose melts at 112–113°, whereas Fischer reported a melting point of 84°. As crystallization seems to be connected with an orientation of the molecules before they separate out of solution, it is likely that for a quick separation the many secondary valences present in the α-biose derivatives prevent an *orientated or crystalline separation,* whereas for the β-bioses this difficulty does not exist in this measure, as their secondary valences have been largely saturated. Crystalline bromo-hepta-acetylmaltose was obtained in pure condition by regulating the time of reaction as described above, thus preventing the

---

[28] Karrer, *Helv. Chim. Acta,* *4,* 169, 263, 678 (1921).

formation of the dibromo derivative, which could not be removed. from the monobromo derivative by recrystallization. Analysis proved that the pure compound had been separated. The crystalline compound is easily soluble in ordinary solvents except petroleum ether and water. It is slightly bitter and was kept for many months without decomposition in a desiccator over sodium hydroxide in the ice box.

Rotation.—Subs., 0.6101: a = +17.640°; $[\alpha]_D^{20}$ = +180.54°. Recrystallization. Subs., 0.3872: a = +11.177°; $[\alpha]_D^{20}$ = +180.24°.

Other preparations gave values near +180.10°, which is taken as the specific rotation of the pure substance.

Anal. Subs., 0.1718: CO_2, 0.2827; H_2O, 0.0808. Subs., 0.2177: AgBr, 0.0581. Calcd. for $C_{26}H_{35}O_{17}Br$: C, 44.62 H, 5.05; Br, 11.43. Found: C, 44.88; H, 5.26; Br, 11.36.

Summary

The pure crystalline fluoro, chloro and bromo derivatives of acetylated melibiose and maltose have been prepared and described. The specific rotational values of these a-biose derivatives show an agreement with the atomic dimension relationship of the monose sugars, whereas the values for the halogen derivatives of the β-bioses, investigated before, agree with this relationship only by excluding the values for the fluoro derivatives. An explanation of this behavior is obtained by model studies, which show that the ***direction*** of the 6-valence allows the constituting monoses to face each other, with a resulting selective influence, whereas the direction of the a-valence does not allow this position. The new (more detailed) structure formula for cellobiose suggests a structure formula for cellulose. As compared with formulas heretofore suggested this new formula gives a better interpretation of the chemical and physical properties of cellulose.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF NAPHTHALIC ACIDS

BY G. J. LEUCK AND R. P. PERKINS WITH FRANK C. WHITMORE

RECEIVED JANUARY 17, 1929 PUBLISHED JUNE 5, 1929

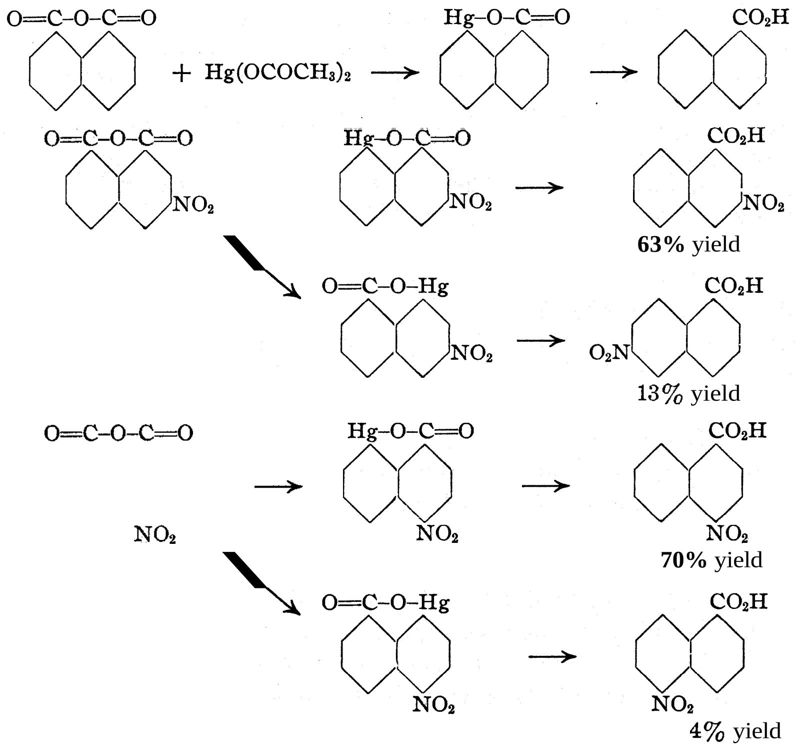
While the replacement by mercury of one of the carboxyl groups in phthalic acid has long been known,[1] the effect of changes in structure on this reaction has not been studied extensively.

In the present study naphthalic acid, 3-nitronaphthalic acid and 4-nitronaphthalic acid have been submitted to the reaction of Pesci. In each case one of the carboxyl groups was replaced by mercury. Naphthalic acid gave anhydro-8-hydroxymercuri-1-naphthoic acid. With 3-nitronaphthalic acid the carboxyl in the 8-position was replaced more than that in the 1-position. With 4-nitronaphthalic acid the replacement was almost entirely in the &position, only a small amount of replacement taking

---

[1] Pesci, *Atti. accad. Lincei,* [5] 10, 1, **362** (1901).

place in the I-position. In each case the products were identified by replacement of the mercury by hydrogen by means of hydrochloric acid.



In addition to the theoretical interest in these reactions they offer the best methods of preparing 3-nitro-1-naphthoic acid and 4-nitro-1-naphthoic acid in a high state of purity and in good yields.

Experimental Part

The **Mercuration** of Naphthalic Acid.—Acenaphthene was oxidized by sodium dichromate in glacial acetic acid.[2] From 100 g. of 75% acenaphthene was obtained 90 g. of purified naphthalic acid (1,8-naphthalenedicarboxylic acid), m. p. 270–271° (85% yield).

A filtered solution of 50.5 g. of naphthalic acid in 1.2 liters of water and 31 g. of sodium hydroxide was mixed with a solution of 55 g. of mercuric oxide in 150 cc. of water and 40 cc. of glacial acetic acid. A slight excess of acetic acid was added and the mixture was refluxed for ninety-eight hours. No more carbon dioxide was evolved and a test sample of the mixture dissolved in sodium hydroxide. The solution gave no metallic mercury when tested with a clean copper wire. The precipitate which had formed was collected on a filter and washed. It was dried at 105°. The yield of anhydro-8-hydroxymercuri-1-naphthoic acid was 84.6 g. (97.6% of the theoretical).

Anal. Calcd. for $C_{11}H_6O_2Hg$: Hg, 54.1. Found: Hg, 52.2, 53.7, 53.4.

---

[2] Graebe and Gfeller, *Ber.*, 25, 652 (1892).

Attempts to purify the anhydro compound were unsuccessful. It is insoluble in organic solvents. Acidification of its alkaline solution gives a gelatinous precipitate which is very difficult to wash and dry.

Sodium 8-hydroxymercuri-1-naphthoate was obtained by evaporating a strongly alkaline solution of the anhydro compound until large white crystals separated on slowly cooling. The crystals were washed with alcohol and dried at 50°.

Anal. Calcd. for $C_{11}H_7O_3HgNa$: Hg, 48.8. Pound: Hg, 48.1, 48.2.

The salt is readily soluble in water containing a little sodium hydroxide. It is readily hydrolyzed by pure water.

A hot solution of 46.5 g. of the sodium salt in 500 cc. of water was treated with 200 cc. of concd. hydrochloric acid and boiled for three hours. The **1-naphthoic** acid obtained was crystallized from hot alcohol; m. p. 162°; wt. 17 g. (87% yield). 1-Naphthoic acid was also prepared from the anhydro compound and hydrochloric acid; yield, 90%.

The Mercuration of **3-Nitronaphthalic** Acid—The anhydride was prepared from naphthalic acid in concd. sulfuric acid solution and solid potassium nitrate at 10–15°.[3] The product after removing impurities with hot toluene (4 cc. per g.) melted at 247–250"; yield, 300 g. from 298 g. of naphthalic anhydride (81% of the theoretical). The pure anhydride was obtained by crystallization from nitrobenzene (225 cc. per 100 g.) or glacial acetic acid (3 liters per 100 g.); m. p. 252–253°.

The anhydride was mercurated in the usual way. From 304 g. of 3-nitronaphthalic anhydride was obtained 505 g. of a mixture of anhydro-3-nitro-8-hydroxymercuri-1-naphthoic acid and the corresponding 6-nitro compound (97% of the theoretical). It is a creamy white powder.

Anal. Calcd. for $C_{11}H_5O_4NHg$: Hg, 48.2. Found: Hg, 48.3.

No way was found for purifying the product.

Sodium 3-nitro-8-hydroxymercuri-1-naphthoate was prepared by dissolving the crude mercurated product in a slight excess of sodium hydroxide and evaporating until crystals separated on cooling. The salt is much less soluble than the corresponding naphthoic compound. It forms large yellow crystals.

Anal. Calcd. for $C_{11}H_6O_5NHgNa$: Hg, 44.0. Found: Hg, 43.3, 43.8.

Sodium **8-Mercuribis-3-nitro-1-naphthoate** ("No. 93").—Starting with 480 g. of naphthalic acid, 70 g. of the desired sodium salt was obtained. The conversion of the hydroxymercuri compound to the mercuri*bis* compound was effected by refluxing with an excess of alcoholic sodium iodide. The product was free of iodides.

Anal. Calcd. for $C_{22}H_{10}O_8N_2HgNa_2$: Hg, 29.6. Found: Hg, 28.9.

Structure of the Mercuration Products.—The mixture of mercury compounds obtained from 3-nitronaphthalic acid was treated with hydrochloric acid for two hours. From 200 g. was obtained 103 g. of a light cream-colored powder (98% of the theoretical). This was dissolved in 1.5 liters of hot glacial acetic acid, filtered from a slight residue and cooled. Fine needle crystals separated, m. p. 265.5°; yield, 65.8 g. (63% of amount theoretically obtainable from the mercurated material). This was nearly pure 3-nitro-1-naphthoic acid. In another run the yield was 60.5 g., m. p. 269–270°. The highest melting point obtained for this acid by repeated crystallization from alcohol was 270.5–271.5°. With smaller runs slightly higher yields were obtained. All the mother liquors were saved for the recovery of 6-nitro-1-naphthoic acid.

Anal. Calcd. for $C_{11}H_7O_4N$: C, 60.8; H, 3.23; N, 6.45. Found: C, 60.5, 60.7; H, 3.09, 3.32; N, 6.39.

---

[3] Graebe and Briones, *Ann.*, 327, 84 (1903).

Ethyl 3-nitro-1-naphthoate was prepared from the acid by thionyl chloride and absolute ethyl alcohol. It formed yellow needles from alcohol and rhombic plates from ethyl acetate, m. p. 87.5–88.5°. The ester did not react with ammonia in water, in alcohol or when fused.

3-Nitro-1-naphthamide was prepared from the acid with thionyl chloride and ammonia, m. p. 264–269°. The amide is difficultly soluble in ethyl alcohol, insoluble in water, difficultly soluble in xylene, slightly soluble in carbon tetrachloride, acetone and benzene, and very soluble in glacial acetic acid. Several crystallizations from ethyl alcohol raised the melting point to 280–280.8°.

Anal. Calcd. for $C_{11}H_8O_3N_2$: N, 12.96. Found: Hg, 12.9.

When 3-nitro-1-naphthamide was treated with sodium hypochlorite or sodium hypobromite, the expected 3-nitro-1-aminonaphthalene was ***not*** obtained.* The products were apparently halogen derivatives of this substance. This behavior was in marked contrast to that of the 6-nitro-1-naphthamide, which gave 6-nitro-1-aminonaphthalene without any complications.

The hydrochloride of 3-amino-1-naphthoic acid was obtained in 90% yield by reducing the nitro compound with sodium hydrosulfite. The preparation of the free amine proved to be very difficult. It was obtained from the hydrochloride in small yields as straw-colored aggregates of needle crystals, m. p. 181–182°.

Anal. (of impure material, m. p. 170–172°). Calcd. for $C_{11}H_9O_2N$: N, 7.49. Pound: N, 7.83.

3-Acetamino-1-naphthoic acid was prepared from the amine and acetic anhydride as cream-colored needles, m. p. 254–255°. The hydrochloride was converted into the known[6] 3-hydroxy-1-naphthoic acid by diazotizing at 0° and pouring into boiling 30% copper sulfate solution. The product extracted with ether melted at about 210°. Two crystallizations from water gave yellow needles, m. p. 228–231°. Purification by sublimation raised the melting point to 239–241° (Royle and Schedler give 242–243°). Solutions in ether, in aqueous alcohol and in benzene have a blue-purple fluorescence. It gives a deep red-brown color with ferric chloride.

The acetyl derivative of 3-hydroxy-1-naphthoic acid was prepared in the usual way, m. p. 172° (Royle and Schedler give 169–170°).

The mother liquors from the crystallization of the mixed acids from 200 g. of the mercury product from 3-nitronaphthalic acid were evaporated to dryness on the steam-bath under reduced pressure; wt., 35 g. This material was treated with 250 cc. of absolute alcohol, saturated with dry hydrogen chloride, refluxed for a short time, allowed to stand for several days, cooled and filtered. The product consisted of lumps of white crystals, m. p. 105–107°; wt., 13.7 g. This was fairly pure ethyl 6-nitro-1-naphthoate. Further crystallization from ethyl alcohol raised the melting point to 111.5–112°. Evaporation of the alcoholic mother liquors gave a mixture of esters of the 3- and 6-nitro compounds which was not further separated.

The ester of 6-nitro-1-naphthoic acid was hydrolyzed to give an acid melting at 207–220°. Several crystallizations from glacial acetic acid raised the melting point to 224–225.5°. Another crystallization from toluene gave the melting point 225–226°. Sublimation gave the highest melting point obtained, 227–227.5°. This was 6-nitro-1-naphthoic acid.

Anal. Calcd. for $C_{13}H_{11}O_4N$: C, 60.8; H, 3.23; N, 6.45. Found: C, 60.7; H, 3.31; N, 6.66.

---

[4] Veselý and Dvořák, *Bull. soc. chim.*, [4] **33**, 327 (1923).

[5] Royle and Schedler, *J. Chem. Soc.*, **123**, 1642 (1923).

6-Nitro-1-naphthamide was prepared in the usual way. Two crystallizations from alcohol gave fine cream-colored needles, m. p. 216.5".

Anal. Calcd. for $C_{10}H_8O_2N$: N, 12.96. Found: N, 13.0.

Treatment with sodium hypochlorite gave **6-nitro-1-aminonaphthalene,** m. p. 172–173° (Veselý and Dvořák, ref. 4, give 167°).

6-Nitro-1-acetaminonaphthalene was prepared, m. p. 237–238° (Veselý and Dvořák give 232–233').

Reduction of the nitro acid by sodium hydrosulfite in 6 N sodium hydroxide gave the known[6] **6-amino-1-naphthoic** acid, m. p. 205.5–206.5° (Harrison and Royle give 203°). An alcoholic solution gives a green fluorescence.

6-Acetamino-1-naphthoic acid was prepared in the usual way. It forms light yellow needles from dilute acetic acid, m. p. 253° (Harrison and Royle give 170–172°).

Mercuration **of 4-Nitro-1-Naphthalic** Acid.—Acenaphthene was nitrated and the nitro compound was oxidized to give 4-nitro-1-naphthoic anhydride.' From 91 g. of 75% acenaphthene was obtained 63 g. of 4-nitro-1-naphthalic anhydride, m. p. 220–224°. Purification through the calcium salt and crystallization from glacial acetic acid raised the melting point to 230'. The anhydride was mercurated in the usual way. The time of refluxing was fifty hours. From 50 g. of the anhydride were obtained 79.7 g. of mercurated product, mainly **anhydro-4-nitro-8-hydroxymercuri-1-naphthoic** acid and a little of the 5-nitro compound.

Anal. Calcd. for $C_{11}H_5O_4NHg$: Hg, 48.2. Found: Hg, 48.4, 48.7.

Treatment of this mixture with hydrochloric acid gave a 95% yield of mixed acids, m. p. 210–218°. Ten g. of the mixed acids on several crystallizations from glacial acetic acid gave 7.1 g. of 4-nitro-1-naphthoic acid, m. p. 225–226'. Repeated attempts to obtain any other acid from the mother liquors failed. The mixed acids were esterified by treatment with thionyl chloride and ethyl alcohol. It was not possible to separate any ester other than the 4-nitro compound.

Ethyl 4-nitro-1-naphthoate and the corresponding methyl ester were prepared from the pure acid; m. p. of ethyl ester, 57–58'; methyl ester, 107.5–108.5°.

The mother liquors from a batch of 4-nitro-1-naphthoic acid were evaporated to dryness; wt., 4 g.; m. p. 216–222°. This was converted to the mixed amides by thionyl chloride and ammonia. After repeated fractionation from dilute ethyl alcohol the insoluble end gave 0.6 g. of **5-nitro-1-naphthamide,** m. p. 230–232°.[8] This corresponded to about 4% of the original mixed acids. A known sample of the 5-nitro-1-naphthamide was prepared from 5-nitro-1-naphthoic acid.[9] A sample of this amide melting at 233–235° was mixed with the amide from the mixed acids. The mixture melted at 230–233°. Recrystallized from benzene the amide melts at 235–236°.

Summary

1. Naphthalic, 3-nitronaphthalic and 4-nitronaphthalic acids were treated with mercuric acetate. In each case one carboxyl was replaced by mercury. With the nitro acids the replacement was mainly in the ring not containing the nitro group.

2. The following mercury compounds were prepared: anhydro-8-

---

[6] Harrison and Royle, J. *Chem. Soc.*, 129, 87 (1926).

[7] Graebe and Briones, *Ann.*, 327, 80 (1903).

[8] 4-Nitro-1-naphthamide melts at 218°. Friedlaender and Weisberg, Ber., 28, 1841 (1895).

[9] Ekstrand, J. *prakt. Chem.*, [2] 38, **276** (1888).

hydroxymercuri-1-naphthoic acid, its sodium salt, sodium 3-nitro-8-hydroxymercuri-1-naphthoate, sodium 8-mercuribis-3-nitro-1-naphthoate and anhydro-4-nitro-8-hydroxymercuri-1-naphthoic acid.

3. Other compounds were prepared, as follows: 3-nitro-1-naphthoic acid, its ethyl ester, its amide, 3-amino-1-naphthoic acid, its acetyl derivative, 6-nitro-1-naphthoic acid, its ethyl ester, its amide, 5-nitro-1-naphthamide.

4. Satisfactory preparative methods were developed for 3-nitro-1-naphthoic acid and 4-nitro-1-naphthoic acid.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CALYCANTHINE. I. THE ISOLATION OF CALYCANTHINE FROM MERATIA PRAECOX

BY RICHARD H. F. MANSKE[1]

RECEIVED JANUARY 17, 1929 PUBLISHED JUNE 5, 1929

The first chemical investigation of the alkaloid, calycanthine, was made by Gordin.[2] He obtained it from Calycanthus glaucus, Willd., and described a convenient procedure for its isolation. In later papers by the same author[3] we are informed that a second lot of seeds, presumably identical with the first, yielded only an isomeric base, namely, isocalycanthine.

Recently a contribution by Spath and Stroh[4] elucidated some obscure points in Gordin's work and established the empirical formula $C_{22}H_{28}N_4$, although the present author is of the belief that $C_{22}H_{26}N_4$ is not entirely excluded.

It was decided to subject the alkaloid to a more rigorous examination and, if possible, to elucidate the relation between calycanthine and isocalycanthine, if indeed the latter has an existence. It may be mentioned that botanists do not appear to be in complete accord in regard to the nomenclature of the various species of Calycanthus, but it may be taken for granted that Calycanthus floridus L., and Calycanthus *fertilis*, Walt. (C. glaucus, Willd.) are two distinct species. From the former the author has isolated about 1.2% of an alkaloid which appears to be identical in all respects with Gordin's calycanthine and also with the base examined by Spath and Stroh.[4] No evidence of the presence of isocalycanthine has been forthcoming although other bases appear to be present in small amounts. The possibility is not excluded that Gordin's second lot of seeds in reality consisted of C. *fertilis*, whereas the first was C. floridus. When the former seeds become available an attempt will be made to determine this point.

---

[1] Holder of the Eli Lilly Company Research Fellowship at Yale University, 1927–1928–1929.

[2] Gordin, THIS JOURNAL, 27, 144, 1418 (1905).

[3] Gordin, *ibid.*, 31, 1305 (1909); 33, 1626 (1911).

[4] Spath and Stroh, Ber., 58, 2131 (1925).

The author was impressed by the fact that so far calycanthine had been found only in plants native to America. Such would be a unique fact, since all other alkaloids found in American plants have been found elsewhere.

The natural order *Calycanthaceae* embraces only two well-defined American and a few Asiatic species, and it was thought that an examination of Asiatic species might reveal the presence of calycanthine or a closely related alkaloid. Actually, it was found that Meratia praecox, Rehd. and *Wils.*, contained mare than 2.5% of calycanthine, identical in all respects with the alkaloid from C. *floridus*. In addition, two other bases were found in minute amount.

The following description was kindly furnished by Mr. John Murray of the Marsh Botanical Garden, Yale University.

Meratia praecox, *Rehd.* and *Wils.* (order Calycanthaceae). Meratia species are often united with *Calycanthus*, but differ in their scaly winter-buds, the yellow flowers appearing long before the leaves on short scaly stalks from axillary buds on branches of the previous year, and in the 5 or 6 stamens. M. praecox is a deciduous shrub growing to a height of 3 meters. The leaves are elliptic-ovate to ovate-lanceolate, 7–15 cm. long, acuminate, bright green and lustrous above, and glabrous beneath. The flowers are about 2.5 cm. broad, very fragrant, the outer sepals yellow, the inner striped purplish-brown; fruit ellipsoid, about 4 cm. long, inclosing several dark brown seeds with a very tough and hard epicarp. Cultivated in China and Japan as an ornamental shrub, and introduced to America in 1766.

Experimental

In a preliminary extraction 50 g. of seeds was ground to a coarse powder and extracted in a Soxhlet extractor with the solvents in the order named.

Solvent	Petroleum ether	Chloroform	Methanol (abs.)	
% of extract	22.7	0.9	18.8	Total, 52.4
Alkaloid isolated	2.6			

The methanol extract was acidified with dilute hydrochloric acid, largely diluted with water, the solution basified and the precipitated alkaloid thoroughly washed with water. The portion soluble in acetone weighed 1.3 g. The petroleum ether and the chloroform extracts contained a further small amount of base.

For the purpose of obtaining the alkaloid in quantity, four kilos of seeds, ground as finely as practicable, was extracted completely with a mixture of 2 volumes of chloroform and 8 volumes of petroleum ether (40–60°). This removed all of the fat, sterols, waxes and a trace of alkaloid.[5] The residue was freed of solvent and extracted in a

---

[5] The examination of the fat has yielded thus far a large amount of unsaponifiable matter, together with an unsaturated acid, presumably oleic, which on hydrogenation yielded stearic acid. It is hoped that the result of a further investigation of this extract, together with that from C. *floridus*, will form the subject of an early communication.

continuous apparatus with absolute methanol. The extract consisted of a dark colored sirupy mass, which was almost completely soluble, but for a small amount of amorphous and gelatinous material, in water made just acid with hydrochloric acid. Filtration offered some difficulty, but treatment of the warm solution with norite tended to coagulate some of the colloidal material and filtration through a layer of norite in a large funnel became possible. The dark brown though clear solution was cautiously basified, and by seeding and scraping the walls of the vessel the crude base was obtained crystalline at once. After a short time it was filtered off, washed with much water and dried. Two recrystallizations from acetone, by the cautious addition of water, yielded **70** g. of pure alkaloid, melting alone or admixed with a specimen from *C. floridus,* at 219–220°.[6] **A** specimen dehydrated by means of potassium carbonate in chloroform melted sharply at 245°. Admixture with a specimen similarly prepared from *C. floridus* did not depress the melting point. Comparison of crystals of the alkaloid from the two sources under the petrographic microscope failed to show any differences.

Examination of the Aqueous Filtrate from the Base.—A small portion of the aqueous alkaline filtrate was acidified with acetic acid, extracted several times with ether, to remove coloring matter, the ether removed by warming, the solution treated with phenylhydrazine and heated on a steam-bath for a short time. The voluminous crystalline precipitate of an osazone was filtered off and washed first with water and then with acetone. It was recrystallized from 95% alcohol and then consisted of the characteristic crystals of glucosazone, which alone or admixed with a genuine specimen melted at **207–208°.**

Isolation of Two Other Bases.—Repeated attempts to isolate other bases by extracting the aqueous solution with immiscible solvents resulted in such a concentration of impurities that only tarry products could be obtained. The following abortive attempt to obtain crystalline water-soluble products resulted in isolating minute amounts of two other alkaloids.

The remaining basic filtrate was treated with a stream of carbon dioxide until neutral and allowed to stand for four weeks. The clear, supernatant liquid was decanted from some residue which had separated and evaporated to a thick sirup under reduced pressure. The latter was extracted once with a liter of 95% alcohol and the solution evaporated. The residue was dissolved in water and sugars were removed by fermentation with yeast. The filtered solution was clarified with basic lead acetate, excess lead was removed by a stream of hydrogen sulfide and the filtrate evaporated to a thick sirup *in vacuo.* The residue was taken up in 95% alcohol, the solution evaporated to dryness and extracted with absolute methanol. This extract was evaporated to a sirup and poured into a large volume of acetone. The acetone solution was evaporated to a thick sirup and extracted repeatedly with boiling ether. The combined ether extracts on being evaporated yielded about **0.5** g. of colorless prismatic crystals, which after one recrystallization from acetone melted at **197–198**" with a slight darkening.

This base, which will be designated a-alkaloid, is sparingly soluble in ether, acetone or water, but readily soluble in dilute acids. The absence of phenolic hydroxyl groups is proved by the insolubility in alkali. A test for nitrogen was strongly positive. With Ehrlich's reagent it gives a beautiful red color, and on heating in a glass tube to a high temperature the odor of indoles becomes apparent.

The mother liquor from the a-alkaloid, from which no more of this base could be obtained, was converted to the hydrochloride and evaporated to a thick sirup. This was extracted several times with boiling chloroform and the extract evaporated. The residue was triturated with a little acetone and then readily crystallized to a magma of microscopic needles. This was filtered off, washed with acetone and recrystallized by

---

[6] Melting points are corrected.

adding acetone to a concentrated alcoholic solution. As thus obtained the hydrochloride melts at 219–220°. Calycanthine hydrochloride melts at 217°, but a mixture of the two began to sinter at 205° and melted completely at 208°. The free base, which will be designated β-alkaloid, was only obtained as a colorless oil, readily soluble in ether. Seeding with a-alkaloid did not induce crystallization. This base also gives a red color with Ehrlich's reagent.

Isolation of Xylose from the Epicarp of the Seeds.—The residue after thorough extraction consisted of the inner fleshy portion of the seed together with the still tough and dark brown epicarp in large flat pieces. By virtue of a difference in density, the two parts could be easily separated by a process of flotation with water, the epicarp sinking. When most of the fleshy portions had been removed by this means, the residue of hulls was hydrolyzed with 2% boiling sulfuric acid for three hours, neutralized with calcium carbonate, filtered, the solution evaporated to a thick sirup *in vacuo* and the latter extracted once with a large volume of absolute methanol. The extract, on evaporation, yielded about 6% of almost colorless crystals which, after two recrystallizations, melted at 150° alone or admixed with a genuine specimen of *l*-xylose. It may here be mentioned that the epicarp from *C. floridus* under similar treatment yielded the same sugar in approximately the same amount.

Summary

1. The alkaloid, calycanthine, has been isolated from *Meratia praecox*, Rehd. and *Wils.*, a shrub native to Asia. Its identity with the alkaloid from *Calycanthus floridus*, L., has been established.

2. Two other alkaloids were isolated in small amounts, but the investigation of these is delayed until more material is available.

3. The existence of glucose, or a sugar which gives glycosazone, in the seeds has been shown.

4. Xylose was isolated from the epicarp of the seeds by hydrolysis with dilute sulfuric acid.

New Haven, Connecticut

[Contribution from the Laboratory of Physical Chemistry, Princeton University]

CHARACTERISTICS OF THE NON-EXPLOSIVE OXIDATION OF PROPANE AND THE BUTANES[1]

By Robert N. Pease[2]

Received January 21, 1929 Published June 5, 1929

The reactions between hydrocarbon vapors and oxygen are of interest for a number of different reasons. Information as to their nature is of

---

[1] This paper contains results obtained in an investigation on "Catalytic Methods Applied to Petroleum Hydrocarbons" listed as Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cohperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

[2] American Petroleum Institute Research Associate, Princeton University.

importance in connection with the utilization of hydrocarbons, especially in connection with their combustion; and from the purely chemical standpoint the mechanism of these reactions demands investigation. Other investigators have studied the oxidation of methane, ethane, ethylene, acetylene and some of the higher paraffins. We have chosen to investigate the oxidation of the intermediate paraffins, propane and the butanes. The investigation has been comprehensive rather than exhaustive. In particular, the nature of the liquid products has been disregarded and conclusions are based entirely on the analyses of gaseous reactants and products.

Apparatus and Procedure

The flow method has been used. Known volumes of reactants at known rates were passed into a reaction tube and the corresponding off-gas collected and analyzed. The gases passed from cylinders through calibrated flow meters (equipped with overflows to maintain constant head) and calcium chloride drying tubes, into $^1/_4$-inch pyrex tubes which extended into the electric furnace used for heating. These tubes were joined within the furnace to a short length of 2-mm. capillary which served as a mixing chamber, and this in turn was joined to the reaction tube. The gases then issued through a length of 2-mm. capillary to which was sealed a three-way stopcock, by means of which communication could be made either with the air or with the collecting system. The latter consisted of a trap of 5-cc. capacity and a 500-cc. mercury aspirator bottle. This was a pyrex flask to which had been sealed a three-way stopcock. The whole of the off-gas was collected in this bottle during a measured time interval, the rate of inflow of reactant gases being controlled by careful regulation of the rate of outflow of mercury from the bottle. During collection of the off-gas, the trap was cooled in carbon dioxide-ether mixture to remove liquid products. Condensable gases were, of course, trapped simultaneously. These were subsequently evaporated by allowing the trap to warm up to room temperature. The gases were then mixed by expansion and compression and submitted to analysis. After analysis the total volume of off-gas was measured and the volumes of the individuals were calculated. All gas volumes were reduced to 25° and 760 mm.

Analysis was carried out with a Williams apparatus to which had been added a copper oxide combustion tube. The confining fluid was water. Carbon dioxide was determined by absorption in potassium hydroxide solution, unsaturated hydrocarbons in dilute bromine water (less than 0.2% of bromine) and oxygen in alkaline pyrogallol. Carbon monoxide and hydrogen were obtained by oxidation with copper oxide at about 300° followed by absorption of carbon dioxide. The saturated hydrocarbons were burned over copper oxide at about 550°, with subsequent absorption of carbon dioxide.

A chromel-wire-wound furnace jacketed with magnesia pipe covering was used. Its interior dimensions were 30 inches length and 4 inches diameter. The wire was wound on a piece of stovepipe covered with asbestos paper. The ends of the furnace were packed with loose magnesia, the central third constituting the actual heating space. Temperatures were measured with a single-junction chromel–alumel thermocouple, the hot junction being at the center of the furnace.

The gases were obtained from cylinders. Their compositions were as follows

Oxygen—O_2, 98.5%; "CH_4," 1.0%; N_2, 0.5%
Nitrogen—N_2, 99.0%; "CH_4," 0.5%; O_2, 0.5%
Carbon dioxide—CO_2, 100.0%
Hydrogen—H_2, 98.5%; "CH_4," 1.0%; O_2, 0.5%

Methane—CH_4, 95.5%; N_2, 4.5%
Propane—C_3H_8, 98.5%; "CH_4," 1.0%; N_2, 0.5%
n-Butane—C_4H_{10}, 99.0%; ["CH_4," (-1.0%)]; N_2, 2.0%
*Iso*butane—C_4H_{10}, 95.5%; "CH_4," 2.0%; O_2, 1.0%; N_2, 1.0%

The boiling points of the normal and isobutane were nearly constant and close to −1 and −10°, respectively, thus further ensuring their purity. These and the other hydrocarbons were originally obtained from natural gas.

The experimental procedure was as follows The furnace was brought to temperature and the gases were allowed to flow through the system for one to two hours to ensure steady-state conditions. The off-gas was then sent through the trap and connecting tubes for one minute. The carbon dioxide–ether mixture was applied to the trap (which was shut off at both ends), and one minute later connection was made through the trap with the gas collector. The whole of the off-gas was then collected for a measured time interval. At the end of this time the trap was warmed to room temperature and the condensed gases were added to the main body, which was mixed and analyzed. The flow rates and sampling times were so adjusted that in all experiments **400** cc. of gas was introduced while the sample was being collected.

Nature of Experimental Data and Interpretation

Analytical Data.—The experimental results have been expressed as follows. The gas absorbed in caustic has been called carbon dioxide. It undoubtedly consists in part of formaldehyde and probably volatile alcohols and acids. Gas absorbed by bromine water has been called simply unsaturated compounds. These are doubtless chiefly olefins. The oxygen, carbon monoxide and hydrogen determinations are unequivocal. The data on saturated hydrocarbons have been expressed in terms of the principal hydrocarbon and methane. This is, of course, arbitrary. Fortunately, however, analyses of the off-gas from the majority of the experiments indicated that the hydrocarbon introduced was the chief one present—no large quantity of new hydrocarbon had resulted from the oxidation. The same holds for the cylinder gases.

We have then to compare the volumes of carbon dioxide, unsaturates, oxygen, carbon monoxide, hydrogen, methane and original hydrocarbon in the off-gas with the volumes of oxygen and hydrocarbon introduced. We find that in general the principal gaseous products of reaction are carbon monoxide and unsaturates, sometimes one and sometimes the other predominating. Methane appears in increasing quantities as the furnace temperature is raised. Hydrogen and carbon dioxide, however, are only rarely important products.

The appearance of unsaturates, methane and hydrogen, all in amounts increasing with the furnace temperature, recalls the dissociation reactions of hydrocarbons, for example

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$C_3H_8 \longrightarrow C_3H_6 + H_2$$

In most experiments, however, furnace temperatures were far below those required to produce appreciable dissociation by themselves; but off-setting this there is the exothermicity of the oxidation reactions. (The question of temperature is discussed below.) We choose therefore to regard the hydrogen and methane as products of dissociation of the hydrocarbon and to associate with them equivalent quantities of unsaturates. We therefore account for a part of the hydrocarbon reacting in terms of thermal dissociation, designating this as "Reaction I. Unsaturates by Dissociation." The amount of this type of reaction is given by the sum of the volumes of methane and hydrogen.

Thermal dissociation as thus evaluated only accounts for a portion of the unsaturates. The remainder must obviously be a product of oxidation. We cannot say what reactions are involved here, but we suggest that they be regarded as oxidations of those portions of the molecules which would be split off in dissociation leaving olefins. Thus, for example

$$\begin{aligned}
C_4H_{10} &\longrightarrow C_4H_8 + H_2 &&\longrightarrow C_4H_8 + H_2O\\
C_4H_{10} &\longrightarrow C_3H_6 + CH_4 &&\longrightarrow C_3H_6 + CH_3OH\\
& &&\longrightarrow C_3H_6 + HCHO, \text{ etc.}\\
C_4H_{10} &\longrightarrow C_2H_4 + C_2H_6 &&\longrightarrow C_2H_4 + C_2H_5OH\\
& &&\longrightarrow C_2H_4 + CH_3CHO, \text{ etc.}
\end{aligned}$$

These then are products of incipient dissociation completed by oxidation of the more saturated product of dissociation. We designate these reactions as of the type "Reaction II. Unsaturates by Oxidation." The amount of this type of reaction is given by the total of unsaturates less the sum of the volumes of methane and hydrogen.

Finally there remains that portion of the reacting hydrocarbon over and above the equivalent of unsaturates produced. In accounting for this we note that in those cases (low temperatures, empty reaction tube) in which little unsaturates, methane and hydrogen are formed, carbon monoxide is produced in amount roughly corresponding to the volume of hydrocarbon consumed, two volumes of oxygen disappearing simultaneously. This appears to be indicative of the type of reaction which Edgar and Pope[3] have found in the case of the higher hydrocarbons and of which an example would be

$$\begin{aligned}
C_3H_8 + O_2 &\longrightarrow C_2H_5CHO + H_2O\\
C_2H_5CHO + O_2 &\longrightarrow CO + H_2O + CH_3CHO, \text{ etc.}
\end{aligned}$$

In any event we take care of the hydrocarbon unaccounted for in Reactions I and II by a third type, an oxidation which is designated "Reaction III. Aldehyde Reaction," The amount of this is obtained by subtracting the volume of unsaturates produced from the volume of hydrocarbon consumed.

We analyze our results then in terms of three reaction types of which the following would be examples: Type I, Unsaturates by Dissociation, *e.* g., $C_3H_8 \longrightarrow C_3H_6 + H_2$; Type II, Unsaturates by Oxidation, *e.* g.,

---

[3] Edgar and Pope, Swampscott Meeting, 1928.

$C_3H_8 + \frac{1}{2}O_2 \longrightarrow C_3H_6 + H_2O$; Type III, Aldehyde Reaction, e. g., $C_3H_8 + 2O_2 \longrightarrow CO(+ CH_3CHO + 2H_2O)$. This establishes a basis for the comparisons of the effects of altering the variables. We do not insist that the possibilities are exhausted by the above types or that the method of calculating the relative amounts is infallible. Methane and hydrogen may well be formed in part by dissociation of intermediate products; the unsaturates may not represent olefins exclusively. Especially, the arbitrary method of representing the hydrocarbons as consisting only of the original and methane doubtless introduces errors. We have, however, a definite basis for the presentation and discussion of the data and we are inclined to think that the scheme and its application are not wide of the mark.

Temperature.—With respect to the reported temperatures, the following is to be kept in mind. These reactions are as a whole exothermic and take place rapidly. Exposure times are of the order of a few seconds. The gases are, therefore, unquestionably at a higher temperature than the surroundings. However, the whole question of temperature under such conditions is decidedly vague. Newly-formed molecules are necessarily highly energized. No matter what the total reaction rate may be, the unchanged molecules with which these product molecules first come in contact are subjected to far more extreme conditions than would correspond to many hundreds of degrees general rise in temperature. Only under such conditions that every newly-formed molecule made many wall collisions before meeting an unchanged molecule would anything corresponding to an isothermal state be set up. In our preliminary work much time was spent in attempting to adjust temperatures down the reaction tube by using a number of independent heating elements. Arrangements were made for determining temperatures at various positions. It was always found, however, that if reaction took place at all, the thermocouple at the entrance to the reaction tube registered from 25 to 50° above that somewhat farther down. We came, therefore, to the conclusion that a better arrangement was simply to place the reaction tube in a constant-temperature bath—the furnace—over its entire length, and to measure and record its temperature. This is at least definite and should be reproducible. The reaction then takes place in a manner that is partly adiabatic and partly isothermal. Since the gases were heated prior to mixing, the recorded temperatures are also the initial temperatures of the reaction mixture.

Heating Time.—Some uncertainty exists as to the exact times of heating in these experiments. When there is no change in the number of molecules on reaction, the temperature is known and constant and the flow is uniform across the reaction tube, the heating time is obtained by dividing the volume of the tube by the flow rate corrected to the temperature and pressure at which reaction is occurring. However, in these reactions, the number of molecules changes on reaction in so far as dissociation is a factor and the actual temperature of the reacting mixture is uncertain. Instead of trying to estimate these effects in separate experiments, and adjusting the flow rate to give a uniform contact time, we have been content to maintain a constant flow rate (measured at room temperature and pressure) throughout any one series of experiments. The average heating time in any series has then been taken as the ideal heating time at a temperature of 472° (745° A., which is $2\frac{1}{2}$ times the average room temperature, 298°). As experiments were conducted over the range 300–625°, this temperature is an average for all experiments. Room temperature might as well have been the basis of calculation, but the above gives more nearly the actual heating times.

The larger empty reaction tube had a volume of 21.6 cc. and the total flow rate at 25° and 760 mm. was 40.0 cc./min. The average heating time was therefore

$$\frac{21.6}{40.0 \times \frac{745}{298}} \times 60 = 13.0 \text{ seconds}$$

The *packed* tube had a volume of 15.8 cc., and the total flow rate was 30.0 cc./min. The average heating time was 12.6 seconds. The results of experiments in the two large tubes are therefore directly comparable as to heating time.

The smaller, empty tube had a volume of 2.6 cc. and the flow rate was 40.0 cc./min. The average heating time was 1.6 seconds. Heating times in this tube are therefore approximately one-eighth as long as in the larger tubes.

The large, empty tube was 1.65 cm. in internal diameter, 11 cm. long with 2-mm. walls. The small empty tube was 0.5 cm. in internal diameter, 10 cm. long with 1-mm. walls. The large, packed tube was 2 cm. in internal diameter, 11 cm. long with 2-mm. walls. It contained 46 g. of broken glass of 6–20 mesh. The glass surface in this tube was 10 to 15 times that in the empty tube.

Results and Discussion

Wall Action.—The first point to be settled was, of course, the influence of the walls of the reaction tube on the reaction. The result was unexpected. In order to determine whether or not the wall material (pyrex glass) catalyzed the reaction, a comparison was made between reactions taking place in an empty tube and in one packed with broken pyrex glass. (The tubes were cleaned with hot concentrated nitric acid and rinsed with water before use.) The result of the comparison was that whereas in the empty tube reaction between oxygen and propane was complete at 375°, in the packed tube there was no reaction below 500°. The glass packing therefore *strongly suppresses* reaction rather than accelerates it, and we must conclude that the walls have a predominantly negative rather than positive catalytic effect. This is in harmony with the observations of Hinshelwood and Thompson on the hydrogen–oxygen combination.[4] Related observations are those of Gautier and Hélier[5] on the explosibility of hydrogen-oxygen mixtures in a tube packed with porous porcelain.

This inhibitory influence of wall surface undoubtedly has to do with the more efficient transfer of energy from the reaction mixture to the surroundings. On the older view the initial temperature is more nearly maintained in presence of the glass packing; on the newer view excited molecules of product are de-activated by the walls instead of transferring excitation to fresh molecules of reactant. We will return to this point later.

There was still the possibility that in addition to this inhibitory influence of wall, which was regarded as physical in nature, the wall material was capable of exerting a positive catalytic effect on the oxidation. If this

---

[4] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)* **118A**, *170* (1928); see also Pease and Chesebro, *Proc. Nat. Acad. Sci.*, *14*, 472 (1928).

[5] Gautier and Hélier, *Compt. rend.*, 122, 566 (1896).

were the case it should be possible to poison the active surface and obtain a further reduction in the amount of reaction. Poisoning the surface amounts to covering it with some material which is itself inactive. Alkali halides suggested themselves as substances which might fulfil this object. Accordingly the tubes were rinsed out with **20%** potassium chloride solution, drained and again put to use. It was found that there was no alteration in the amount of reaction of oxygen and propane in the empty tube. In the packed, "coated" tube, however, the temperature at which reaction began was raised from around **500** to 575°, and reaction was still incomplete at 625°, whereas prior to coating it had been nearly complete at 550°. We have then to deal not only with an inhibitory action of the walls but also with a positive catalytic effect which, however, can be markedly decreased (and possibly eliminated) by poisoning. In the large, empty tube, on the other hand, we are safe in assuming that the observed reaction is almost exclusively homogeneous.

We will designate the reaction taking place in the large, empty, coated tube as the "free reaction," and that in the large, packed, coated tube as the "inhibited reaction." It is of interest to consider these two in some detail. Because it is in some respects the simpler and more normal of the two, the inhibited reaction will be first discussed.

The Inhibited Reaction

Propane.—Data on the reaction between propane and oxygen in the packed, coated tube are given in Table I. (In all these experiments close to **400** cc. of gas was introduced while the sample of off-gas was being collected, the actual amount being, of course, used in the calculations. For the sake of clearness, the amounts in round numbers are entered in

TABLE I

REACTION OF PROPANE AND OXYGEN IN PACKED, COATED TUBE

Temp., °C.	Gas in, cc. O_2	Gas in, cc. C_3H_8	Reacting, cc. O_2	Reacting, cc. C_3H_8	Formed, cc. Unsats.	Formed, cc. CH_4	Formed, cc. H_2	Formed, cc. CO	Formed, cc. CO_2	% C_3H_8 introduced to reaction. I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
575	300	100	8	13	4	3	2	1	1	5	0	8	13
600			33	27	20	1	4	5	2	5	15	7	27
625			35	32	25	14	3	2	2	17	8	7	32
575	100	300	6	27	14	10	1	1	1	4	1	4	9
600			39	78	64	33	3	3	2	12	9	5	26
625			84	144	119	105	1	3	5	35	4	8	47
	N_2												
600	100	300		33	22	32	3			11			11
625				45	40	32	17			15			15
					Before coating with KC1								
	O_2												
550	300	100	287	88	15	8	13	167	49	15	0	74	89
	100	300	95	146	101	58	11	41	6	24	11	15	50

the tables under "Gas in." In addition, the temperature, volumes in cc. of hydrocarbon and oxygen reacting and of gaseous products formed and the percentages of total hydrocarbon introduced which have reacted according to the reaction types in which the results have been expressed are given.)

The first point to be noted is that approximately the same fraction of propane reacts whether the initial propane–oxygen ratio is 3 to 1 or 1 to 3. The conversion of propane is therefore approximately first order with respect to its own concentration. Since a large proportion of what reacts appears as dissociation products, one might suspect that the chief reaction was a purely thermal dissociation. When, however, nitrogen is substituted for oxygen as diluent, it is found that only one-third to one-half as much propane reacts. Hence it is clear that the dissociation has been for the most part excited by the simultaneous oxidation reactions. It is nevertheless significant that one has to approach conditions conducive to thermal dissociation before any reaction occurs. The oxidation reaction is evidently contingent on the possibility of dissociation, and at the same time promotes dissociation. It is as though the underlying reaction were still the unimolecular dissociation of the hydrocarbon but that the degree of activation requisite for reaction were lowered.

It is to be noted that little if any carbon monoxide, carbon dioxide or hydrogen is formed. Since less hydrogen is obtained from the oxidation than from the dissociation, it is evident that some has been burnt—under circumstances, it may be added, such that little hydrogen alone would have reacted. There is fairly clear indication here of removal of hydrogen directly from the hydrocarbon molecule by oxidation. This was given as an example of one of the type reactions, and for this reason. The absence of carbon monoxide and carbon dioxide shows that such carbon-oxygen linkages as have been formed have issued in liquid products. The marked difference in this respect between experiments before and after coating with potassium chloride will be noted.

It is a peculiarity, attributable to the unimolecular character of the reaction, that more oxygen is consumed from the mixture which is deficient in oxygen. It should be noted also that the mixtures richer in oxygen, although the more explosible because of their greater potential energy content, are under these conditions the less reactive.

The Free Reaction

Propane.—We turn now to a consideration of the very different type of reaction between propane and oxygen which takes place first at 300–400° (as compared to 575–600°) in our larger, empty tube. Carbon monoxide is now the principal gaseous product. The reaction is of a highly spontaneous character and gives every evidence of being of the chain type. Results are presented in Table II.

TABLE II

REACTIONS OF PROPANE AND OXYGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reastion,			
	O_2	C_3H_8	O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
300	300	100											
325			Nil		Nil								
350			119	51	10	0[a]	9	59	14	9	1	43	53
375			115	50	17	0	4	58	11	4	14	34	52
400			97	44	16	0	9	50	9	9	7	29	45
425			67	42	19	0	4	35	5	4	15	24	43
450			Explosive										
300	200	200	Nil		Nil								
325			183	98	20	3	4	91	15	4	7	41	52
350			192	100	24	0	3	90	17	2	11	40	53
375			193	105	31	0	11	95	14	6	11	38	55
400			187	107	37	4	5	92	11	5	15	36	56
425			Explosive										
300	100	300	Nil		Nil								
325			93	66	15	2	5	45	6	2	3	18	23
350			96	70	24	5	6	45	5	4	4	16	24
375			94	74	27	8	5	40	4	5	5	17	27
400			94	81	37	8	6	40	5	5	8	15	28
450			94	101	63	15	12	40	5	9	12	13	34
500			93	137	91	48	12	48	5	21	11	16	48
550			96	151	109	53	19	51	4	25	13	15	53
600			94	178	131	81	33	54	3	40	6	16	62
Before coating with KCl													
375	300	100	124	49	15	0	6	56	11	6	9	35	50
	200	200	189	99	30	1	11	88	13	6	9	36	51
	100	300	93	73	32	6	7	39	4	5	7	14	26

[a] In these and many other experiments with excess of oxygen, the saturated hydrocarbon in the off-gas averaged slightly higher in carbon than the original hydrocarbon. There would thus be no indication of the presence of methane. Small quantities of saturated hydrocarbons of higher molecular weight than the original appear to be formed under these conditions. The discrepancy never exceeded a few cc. and no attempt has been made to allow for it.

The reaction does not follow any conventional scheme. It starts abruptly within a 25° temperature interval, and, in the case of the $3C_3H_8{:}1O_2$ and $2C_3H_8{:}2O_2$ mixtures, runs immediately to complete consumption of the oxygen. Somewhere between $C_3H_8{:}O_2$ ratios of 2:2 and 1:3 there is another abrupt change such that at the lower propane concentrations only one-half to one-fourth of the oxygen reacts, although the start of reaction as the temperature is raised is still abrupt. Moreover, the reaction has under such conditions a quite definitely negative temperature coefficient, although it eventually becomes mildly explosive.

At first sight the diminished reactivity of mixtures low in propane appears to be in harmony with the results of the corresponding experiments in the packed tube at higher temperatures. There is, however, more than a suspicion that in the empty tube excess of oxygen rather than deficiency of propane is the important factor in limiting the reaction. Experiments were carried out in which one-third of the oxygen of the $1C_3H_8:3O_2$ mixtures was replaced by some other gas giving mixtures of the composition $1C_3H_8:2O_2:1$ diluent. The diluent gases were nitrogen, carbon dioxide, methane and hydrogen. Results are presented in Table III.

TABLE III

EXPERIMENTS ON MIXTURES OF COMPOSITION $1C_3H_8:2O_2:1$ DILUENT IN THE LARGER, EMPTY, COATED TUBE

Gas in, C_3H_8, 100 cc.; O_2, 200 **cc.; diluent,** 100 **cc.**

Temp., °C.	Diluent	Reacted, cc. O_2	Reacted, cc. C_3H_8	Formed, cc. Unsats.	Formed, cc. CH_4	Formed, cc. H_2	Formed, cc. CO	Formed, cc. CO_2	% C_3H_8 introduced to reaction, I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
375	O_2	115	50	17	0	4	58	11	4	13	34	52
	CH_4	109	53	15	0	3	47	8	3	12	39	54
	N_2	109	47	14	0	6	45	9	6	8	35	49
	CO_2	94	46	13	0	4	45	(15)	4	9	35	48
	H_2	93	42	12	0	(2)	47	8	(2)	(10)	31	43
425	O_2	67	42	19	0	4	35	5	4	15	24	43
	CH_4	31	19	13	0	3	12	1	3	10	6	19
	N_2	11	12	10	0	1	8	1	1	9	2	12
	CO_2	12	8	6	0	4	7	(11)	4	2	2	8
	H_2	Nil										

The substitution of diluent for part of the oxygen makes very little difference in the amount of reaction at 375°. There is a small decrease in the order O_2, CH_4, N_2, CO_2, H_2. At 425°, however, this effect becomes so pronounced that, in the presence of hydrogen, reaction is almost entirely suppressed. These diluent gases clearly have specific inhibitory effects on the oxidation, the effect being more pronounced at the higher temperature. The similarity of the results when oxygen is the diluent leaves little room for doubt that this substance itself is as well inhibitor as reactant, and especially that the negative temperature coefficient observed with excess of oxygen is intimately related to the inhibitory action of this substance. That propane does not have a similar effect may be seen by comparing the results of experiments with $2C_3H_8:2O_2$ mixtures (Table II) with the above.

So far as is known, no similar observations on homogeneous gas reactions have been noted except those involved in anti-knock action, which refer, of course, to precisely this type of reaction—the oxidation of hydrocarbons.

The characteristics of the free reaction convince us that we are dealing with a chain mechanism. The reactions in question are undoubtedly those suggested by Edgar and Pope[3] as the reactions of oxidation of the higher paraffins, and may be represented by the equations

$$C_3H_8 + O_2 \rightarrow C_2H_5CHO + H_2O$$
$$C_2H_5CHO + O_2 \rightarrow CH_3CHO + H_2O + CO, \text{ etc.}$$

In the case of propane the two reactions written above appear to be chiefly concerned, since in general we obtain 1 mole of carbon monoxide for 1 mole of propane and 2 moles of oxygen reacting. This is the sequence of reactions which is suppressed by diluents and KCl-coated, glass packing, and which has the chain mechanism. These reactions induce those yielding unsaturates and are the more effective in this respect as the temperature is raised.

Further information as to the nature of the free reaction is given by experiments in which 50% propane–oxygen mixtures were diluted with nitrogen. Results are presented in Table IV.

TABLE IV

REACTION OF 50% PROPANE–OXYGEN MIXTURES DILUTED WITH NITROGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in cc. N_2	O_2	C_3H_8	Reacted, cc. O_2	C_3H_8	Formed, cc Unsats.	CH_4	H_2	CO	CO_2	% C_3H_8 introduced, to reaction. I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
350	300	50	50	Nil										
375														
450														
500				28	27	16	0	0	12	1	0	33	23	56
550				46	40	22	1	4	28	3	10	35	37	82
600				48	37	24	12	3	35	3	32	19	28	79
300	200	100	100	Nil										
350				73	39	9	0	4	3	3 6	4	5	32	41
400				Nil										
450				Nil										
475	Slightly explosive			76	62	37	14	17	50	6	33	6	26	65
300	100	150	150	Nil										
350				138	69	16	0	1	69	11	1	10	37	48
400				75	53	21	0	3	31	4	2	13	23	38
350	300	50	50	Nil										
	200	100	100	73	39	9	0	4	3	3 6	4	5	32	41
	100	150	150	138	69	16	0	1	69	11	1	10	37	48
	0	200	200	192	100	24	0	3	90	17	2	11	40	53
400	300	50	50	Nil										
	200	100	100											
	100	150	150	75	53	21	0	3	31	4	2	13	23	38
	0	200	200	187	107	37	4	5	92	11	5	15	36	56

Results with mixtures containing 50% nitrogen are particularly striking. Considerable reaction took place at 350°, but not at 300, 400 or 450°. At 475° the mixture became very mildly explosive but a sample could still be taken. The reaction rate first increases with temperature (300–350°), then decreases to zero (350–450°) and finally again increases (450–475°). When the nitrogen content is increased to 75% the whole of the low temperature reaction is wiped out, and only the higher temperature region (500–600°), with its positive temperature coefficient but without the explosive character, remains. It is to be noted that when reaction does set in, the formation of unsaturates is considerable as compared to that of carbon monoxide. This is equally true for the 50% mixture at 475°.

We have seen that the reactions of propane and oxygen can be suppressed by dilution or by the use of a KCl-coated glass packing. It was desired to determine the effect of shortening the heating time. To accomplish this it was convenient to keep the flow rate the same and use a smaller reaction tube. Accordingly a tube of the same length as the larger, empty tube (about 11 cm.) but of about one-third the diameter (0.5 cm. as against 1.6 cm.) was made up. Results are given in Table V.

TABLE V

REACTION OF PROPANE AND OXYGEN IN THE SMALLER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	O_2	C_3H_8	O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
600	300	100	12	10	11	0	7	4	1	7	4	0	11
625	Explosive												
500	100	300	Nil										
550			25	48	38	19	0	1	3	6	6	3	15
600			93	150	125	58	17	36	6	26	17	9	52

Reaction is again forced into the higher temperature region with the formation of unsaturates predominating.

The heating time in this smaller tube was one-eighth of that in the larger tube. This would be expected to decrease the amount of reaction correspondingly; but the observed decreases are so great as to warrant the conclusion that the decrease in tube diameter is effective of itself. Reaction only sets in at 500-600° instead of at 300–400°. In the smaller tube contact between gas molecules and the tube walls is facilitated. Apparently the difference in this respect between the smaller and larger tubes is sufficient to give the observed marked differences in reaction characteristics.

There is finally one more way in which the propane–oxygen reactions can be affected. This is by reducing the pressure. Experiments were carried out in which hydrocarbon–oxygen mixtures were caused to flow through a tube of large volume at 5 to 10 mm. pressure. The quantitative results were not very satisfactory owing to irregularity. Qualitatively, however, there was no question but that the suppression of reaction was very great. No reaction whatever took place below 600°. At higher temperatures there was certainly a parallelism between the amounts of hydrocarbon dissociating in nitrogen and the amount reacting in oxygen. It was not possible to conclude whether the same amount of hydrocarbon was involved in the two cases, or whether the two reactions were independent of each other. Once more, however, we find reaction finally setting in under conditions which are favorable to dissociation alone.

What has been said of the low pressure oxidation of propane applies as well to that of the butanes and aiso of ethane.

In the oxidation of propane we have then to deal with three types of reaction—that yielding unsaturates, and methane or hydrogen by dissociation, that yielding unsaturates and unidentified liquid products by oxidation and that yielding carbon monoxide and unidentified liquid products (again by oxidation). The first two types always appear together, sometimes one and sometimes the other predominating, and increase in amount as the temperature is raised. Unless the carbon monoxide reaction is taking place (as in the larger, empty tube) the reactions yielding unsaturates do not put in an appearance until the temperature reaches 550–600°. They give evidence of being more or less normal homogeneous gas reactions, first-order with respect to propane, which are subject to excitation by the carbon monoxide reaction in amount which is small at the lower temperatures but increases as the temperature is raised.

In the carbon monoxide reaction we meet with a wholly different state of affairs. This reaction is promoted by excess of hydrocarbon but depressed by excess of oxygen. Dilution with other gases than oxygen likewise inhibits the reaction; the extent of inhibition is a specific property of the diluent, and suppression by any of the diluents (including oxygen) is greater at higher temperatures so that the reaction under these conditions has a negative temperature coefficient. This reaction is likewise suppressed by a glass packing, particularly when this is coated with potassium chloride; it is suppressed in reaction tubes of small diameter; and it is suppressed when the pressure is lowered to a few millimeters. These are characteristics to be expected of a chain reaction, and we do not hesitate to state that a chain mechanism is here involved.[6] We have, however, no evidence bearing on the nature of the chain, though the formation of aldehydes and the possibilities of peroxide formation are to be borne in mind.[7]

That the reactions are as a whole exothermic is shown by the fact that a jacketed thermocouple will register a temperature 25–50" higher in a small region close to the inlet end than in the rest of the tube. A spontaneous development is not surprising. Rather, what requires explanation under these circumstances is the fact that other possible reactions

---

[6] We have recently found that this reaction is also faintly luminous.

[7] See Mardles, J. Chem. *Soc.,* 133,872 (1928)

are not more influenced, in particular, the fact that the excess of hydrocarbon which is always present is not more radically and more completely decomposed. The evidence is all in favor of the conclusion that the reaction energy is not as a whole available for heating the gases but is largely retained in some special form by product molecules to be given up to the walls or to be devoted by a specific mechanism to the continuance of the particular reaction to which it is due.

Reactions of the Butanes with Oxygen.—It remains now to present data on the reactions of the butanes with oxygen under conditions corresponding to those of the propane–oxygen reactions which have aready been presented and discussed in detail. The relations are essentially the same as with propane. Reaction is in general more ready and suppression is more difficult. Of the two, n-butane is the more reactive.

The Inhibited Reaction.—Results with the packed coated tube are presented in Table VI.

TABLE VI

REACTIONS OF THE BUTANES AND OXYGEN IN THE PACKED COATED TUBE

Temp., °C.	*Gas in, cc.* O_2	H.C.	*Reacted, cc.* O_2	H.C.	*Formed, cc.* Unsats.	CH_4[a]	H_2	CO	CO_2	*% H. C introduced to reaction,* I *unsats. by dis.*	II *unsats. by ox.*	III *aldehyde reacts.*	*Total*
					Isobutane								
450	300	100	40	14	11	0	4	10	8	4	7	3 1	4
500			109	42	22	0	3	42	18	3	20	21	44
550			197	69	31	14	11	106	24	26	6	40	76
450	100	300	45	25	28	0	6	8	1 1	2	8	0 1	0
500			87	73	63	23	3	15	15	9	13	3	25
550			97	107	89	74	2	5	12	27	5	6	38
					n-Butane								
400	300	100	56	15	11	4	4	7	7	8	3	4 1	5
450			140	46	20	0	4	46	33	4	15	26	45
500			183	63	31	8	7	80	33	15	16	33	64
400	100	300	Nil										
450			58	35	34	9	1	4	15	3	8	0 1	1
500			88	85	78	22	6	23	17	10	17	**2**	29

[a] The interpretation of the analyses for saturated hydrocarbons in the off-gas are the more uncertain in these cases because of the probability that ethane is also present.

A comparison of these with the corresponding results for propane shows that whereas the latter only reacted at 600° with very little carbon monoxide formation, the butanes are reacting at 500° and considerable carbon monoxide is produced. The packing, therefore, does not repress the "aldehyde reaction" so readily in these cases. A finer packing might perhaps be more effective. As between the two, reaction development is the more ready in n-butane but the differences are not great, particularly when oxygen is in excess.

The Free Reaction.—Reaction between the butanes and oxygen in the larger, empty, coated tube takes place in a manner not very different from that with propane. A greater proportion of oxygen is consumed and reaction passes more readily into explosion. Indeed, *n*-butane–oxygen mixtures of composition 2:2 or 1:3 showed no region of quiet reaction. Results are presented in Table VII.

TABLE VII

REACTIONS OF THE BUTANES AND OXYGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.			Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	diluent	O_2	H. C.	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
						Isobutane								
350	None	300	100	181	62	12	0	5	75	17	5	7	52	64
400	Explosive													
350	None	100	300	100	60	29	4	0	37	6	1	9	11	21
400				98	77	39	11	0	34	6	4	10	13	27
450				100	100	68	33	9	41	7	15	9	11	35
400	N_2, 100	200	100	149	51	16	0	4	59	14	4	13	37	54
	H_2, 100	200	100	160	61	14	0	6	68	10	6	8	49	63
425	Both diluted mixtures explosive													
						n-Butane								
Mixtures of 100 C_4H_{10}–300 O_2 or 200 C_2H_{10}–200 O_2 have no zone of quiet reaction														
350	None	100	300	93	64	30	26	6	36	9	10	0	12	22
450				96	91	77	42	7	39	12	17	10	5	32

With 3:1 hydrocarbon–oxygen mixtures (when all of the oxygen is consumed) the proportions of reactants and products are much the same as with propane. The 1:3 *iso*butane–oxygen mixture reacts only incompletely when it does not explode (e. g., at 350°) as in the case of the cor-

TABLE VIII

REACTIONS OF THE BUTANES AND OXYGEN IN THE SMALLER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	O_2	H. C.	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
					Isobutane								
500	300	100	43	15	15	0	2	14	5	1	14	0	15
550	Explosive												
450	100	300	22	13	18	0	0	0	5	0	7	0	7
500			54	52	46	5	0	9	7	2	14	2	18
550			99	116	101	39	8	32	9	16	19	5	30
					n-Butane								
450	100	300	70	49	42	4	2	17	13	2	12	4	16
500			70	75	68	10	4	16	13	5	18	2	25
550			93	124	130	53	8	32	12	20	21	0	41

responding propane mixture, though a greater proportion of the oxygen is consumed. There is less indication of suppression by diluents, however. Data referring to the smaller, empty, coated tube are given in Table VIII.

It is seen that in the smaller, empty, coated tube the butanes again react more readily than propane, and that *n*-butane is the more reactive of the two. In this case the system of interpretation appears to be strained somewhat by the appearance of excessive quantities of unsaturates. It is possible that the formation of ethane is responsible, or that in some cases two molecules of ethylene are formed from one of butane.

A comparison between the amounts of reaction of 3:1 butane–oxygen mixtures at 450° in the larger and smaller empty tubes is available and is of some interest. It will be recalled that the two tubes give heating times in the ratio of 1 to 8 (1.6 and 13 sec., respectively) their diameters being in the approximate ratio of 1 to 3. Results are given in Table IX.

TABLE IX

COMPARISON OF 3:1 BUTANE–OXYGEN MIXTURES AT 450° IN SMALLER AND LARGER, EMPTY, COATED TUBES

Tube	Reacted, cc.		Formed, cc.					C_3H_8 introduced to reaction, %			
	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
					Isobutane						
Small	22	13	18	0	0	0	5	0	7	0	7
Large	100	100	68	33	9	41	7	15	9	11	35
					n-Butane						
Small	70	49	42	4	2	17	13	2	12	4	16
Large	96	91	77	42	7	39	12	17	10	5	32

The differences are ascribed to an increase principally in the amounts of dissociation, along with a considerable increase in the amount of carbon monoxide, which, however, does not appear in the analysis of results as due to our aldehyde reaction, though doubtless this would be the correct interpretation.

We conclude that there is no essential physico-chemical difference between the reactions of the butanes with oxygen and those of propane and that the same considerations are applicable. This being the case, we are inclined to believe that the same will be true of the higher hydrocarbons. Differences will necessarily appear in the study of the lower hydrocarbons, methane and ethane, because of the impossibility of certain types of reaction, and these will require special study. The appearance of carbon monoxide and water as the principal products of methane oxidation is suggestive of a similarity in some sense. In the case of ethane the slowness of the reactions when oxygen is in excess, as shown by Bone and Stockings,[8] is exactly in accord with results found for propane and the

---

[8] Bone and Stockings, J. Chem. *Soc.*, 85,693 (1904).

butanes. It may be added that Bone and Wheeler[9] and Bone and Andrew[10] find the same effect in the slow oxidation of ethylene and of acetylene, pointing to chain mechanisms in these cases also.

These results are admittedly incomplete. What was aimed at was a survey of the field. The points that will interest us especially in further investigations are the nature of the chain reaction and especially of the diluent effect, and the behavior of the lower hydrocarbons.

It may be pointed out that the indications are that liquid products containing the same number of carbon atoms as the original hydrocarbon are not formed in quantity. The aldehyde with one less carbon atom should be obtainable in a fairly pure state by oxidation at the lowest possible furnace temperature with excess of hydrocarbon. High temperatures and the maximum suppression give good yields of what are undoubtedly olefins, under conditions which are more convenient than those required for ordinary dissociation. In fact, this is unquestionably a suitable method to prepare olefins from saturated hydrocarbons. We have no very clear ideas as to the nature of the reactions producing unsaturates by oxidation except that the burning off of hydrogen to give the olefin of the same chain length is one reaction, and that reactions such as

$$C_3H_8 + {}^1/_2O_2 \rightarrow C_2H_4 + CH_3OH$$

$$C_3H_8 + O_2 \rightarrow C_2H_4 + HCHO + H_2O$$

are possible. We are inclined to believe that the formation of alcohols, which probably occurs, is referable to the first of these reactions and may be regarded as due to the tendency of the hydrocarbon to undergo demethanation. The formation of acids is perhaps due to secondary oxidation of aldehydes but we have no evidence on this point for or against.

There is no question but that the proportions of these various reactions can be altered profoundly by relatively minor changes in the methods of carrying out the oxidation. This is to be borne in mind by those interested in arriving at a more precise idea of the nature of the liquid products, or in forcing the reactions in some one particular direction. One point in particular is worth bearing in mind. Probably any catalyst will act to suppress what we have called the aldehyde reaction just as a glass packing does. On top of this effect will be superimposed the specific action of the particular catalyst employed. The role of the catalyst will thus be always a dual one.

Summary

1. A study has been made by the flow method of the reactions of mixtures of oxygen with propane and the butanes. No attempt has been made to analyze the liquid products and all conclusions are based on the results of gas analyses.

---

[9] Bone and Wheeler, on ethylene, *J. Chem. Soc.*, **85**, **1637** (1904)

[10] Bone and Andrew, on acetylene, *ibid.*, **87**, **1232** (1905).

2. The reactions are classified into three types, which (with examples) are as follows: (I) Unsaturates by Dissociation, Example—$C_3H_8 \longrightarrow C_3H_6 + H_2$; (II) Unsaturates by Oxidation, Example—$C_3H_8 + {}^1/_2O_2 \longrightarrow C_3H_6 + H_2O$; (III) Aldehyde Reaction, Example—$C_3H_8 + 2O_2 \longrightarrow CO + 2H_2O + CH_3CHO$.

3. Types I and II give evidence of being more or less normal homogeneous gas reactions which appear at 500–600°, but are subject to induction by Type III at lower temperatures in amount increasing with the temperature.

4. Type III may begin at temperatures of 300–350° and gives every indication of being a chain reaction. Its development is highly spontaneous, and at the same time it is sensitive to relatively minor variations in the conditions of reaction. In particular, it is subject to suppression by a broken-glass packing (especially when this is coated with potassium chloride), and by use of a reaction tube of small diameter. Lowering the pressure to a few millimeters has a like effect. Dilution with oxygen, methane, nitrogen, carbon dioxide or hydrogen depresses the reaction in amount increasing in the order named; this effect is the greater at higher temperatures. Under these conditions the reaction thus has a negative temperature coefficient, though eventually becoming explosive. Excess of hydrocarbon promotes the reaction.

5. Under suppression, there may be no reaction up to 500–600°. Types I and II then appear, accompanied by Type III in varying amount.

6. Considerations bearing on the isolation of particular reactions are set forth.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 222]

THE STRUCTURE OF METAL KETYLS. I. THE SCHMIDLIN FORMULA

BY CHARLES BUSHNELL WOOSTER[1]

RECEIVED JANUARY 23, 1929 PUBLISHED JUNE 5, 1929

The highly colored products formed by the addition of one atom of an alkali metal to one molecule of certain aromatic ketones were named "metal ketyls" by Schlenk and his co-workers,[2] who concluded that these substances comprised a new class of compounds containing trivalent carbon. This view was criticized by Schmidlin,[3] who contended that they should be regarded as molecular compounds analogous to those formed between

---

[1] National Research Fellow

[2] (a) Schlenk and Weikel, Ber., 44, 1182 (1911); (b) Schlenk and Thal, *ibid.*, 46, 2840 (1913); (c) Schlenk, Appenrodt, Michael and Thal, *ibid.*, 47, 486 (1914).

[3] Schmidlin, "Das Triphenylmethyl," Stuttgart, 1914, pp. 186–188.

the ketones and metal chlorides[4] and could best be represented by the formula RR′C═O···Me.

Such a formula has little or no definite significance until the meaning of the symbols employed (particularly the dotted line) has been defined in terms of the properties to be expected of the substance represented. In his consideration of the reactions of these compounds Schmidlin gave a very clear definition of the meaning of his formula. In every case he assumed that a dissociation into the ketone and free metal occurred, and was immediately followed by interaction of the latter with the reagent employed. When the product of this interaction was capable of reacting further with the ketone, derivatives were obtained which were identical with those resulting from a mixture of the ketone, the reagent and the alkali metal. Otherwise, the entire amount of ketone was recovered at the end of the reaction.

The mechanism proposed by Schmidlin for the reaction between metal ketyls and alkyl halides may be subjected to a very exacting test by carrying out this reaction in the presence of some additional reagent capable of reacting with any intermediate organo-alkali products which might be formed. A suitable material is liquid ammonia and its influence upon this reaction has been studied under conditions permitting the collection of all gases formed in the process. Two trials gave identical results; only a negligible quantity of gas insoluble in water was collected. If sodium ethyl[5] had been formed as an intermediate step, reaction with the ammonia would be expected, resulting in the formation of ethane

$$C_2H_5Na + NH_3 \longrightarrow NaNH_2 + C_2H_6 \qquad (1)$$

Furthermore, if dissociation of the ketyl into ketone and free metal had occurred, as Schmidlin supposes, the formation of ethane might be expected in any event, for this gas has been shown to be a product of the action of ethyl iodide on sodium in liquid ammonia.[6]

The only assumption that can harmonize these results with the Schmidlin formula is that a competition occurs between the ketone and the solvent ammonia in their reactions with the product formed from sodium and ethyl bromide and that the reaction with the ketone preponderates because of its greater rapidity. The validity of this assumption was then tested by adding metallic sodium to a solution of benzophenone and excess ethyl bromide in liquid ammonia. Ethane, in an amount equivalent to the sodium used, was evolved in both of the experiments carried out.

The Schmidlin formula, as defined and interpreted by its author, requires that the action of ethyl bromide on the ketone–metal compound

---

[4] (a) Pfeiffer, *Ann.*, **383**, 97 (1911); (b) K. H. Meyer, *Ber.*, 42, 1149 (1909); 43, 157 (1910).

[5] Schmidlin actually suggested a complex of the type C_2H_5NaBr.

[6] Lebeau, *Compt.* rend., 140, 1043 (1905).

and that of the metal itself on the ethyl bromide–ketone mixture be identical. The fact that these two reactions lead to quite different results in the presence of liquid ammonia demonstrates conclusively that *the Schmidlin formula is incorrect.*

However, the interpretation of the reactions of these compounds proposed by Schlenk and his co-workers is not the only alternative to be considered. For instance, it has been observed that monosodium benzophenone results from the action of benzophenone upon its disodium derivative in liquid ammonia

$$(C_6H_5)_2C(Na)ONa + (C_6H_5)_2C{=}O \longrightarrow 2\ (C_6H_5)_2CONa \qquad (2)$$

If it is assumed that this reaction is to some extent reversible and that under the influence of any reagent which attacked the very reactive sodium atom in the disodium compound, the transformation could be caused to proceed to completion in the sense of Equation 2 as read from *right* to *left;* it would be expected that the products would consist of the ketone and of the equivalent of an equimolecular quantity of the di-metallic derivative in the form of the materials ordinarily resulting from the action of the reagent upon it. It is a noteworthy fact that the substances actually isolated and identified after decomposition of the ketyls with numerous reagents have been identical with those which are thus predicted, with the single exception that in certain instances the products of hydrolysis of the solid also contained a quantity of the pinacol; this may be ascribed to partial polymerization of the ketyl to the pinacolate. These considerations are of particular significance since they suggest that none of the reagents hitherto employed attack the ketyls *directly* and consequently such reactions scarcely reveal the structure of the ketyls themselves.

Experimental Part

Apparatus.—A diagram of the apparatus used in these experiments appears in Fig. 1. A pyrex reaction tube A fitted with two ground-in introduction tubes B was attached to the system with de Khotinsky cement. It could be evacuated by means of a mercury vapor pump and ammonia introduced from a cylinder attached at C. This cylinder, which is not shown, was filled with liquid ammonia from a commercial fifty-pound tank, a few pieces of sodium metal having been previously introduced. Ammonia thus dried was always used as the solvent for the reacting materials and was transferred from the cylinder by distillation. A manometer D permitted the pressure within the tube to be regulated so that pure ammonia could be condensed therein when it was surrounded by a cylindrical Dewar flask containing a bath of commercial liquid ammonia. The ammonia which was allowed to evaporate at the end of a reaction was permitted either to escape through outlet E into a carboy of water, or could be passed into the gas-collection tube F. This tube contained water for the absorption of ammonia and the volume of any insoluble gas which collected in the tube could be measured. Fresh water could be introduced through a tube which led to the upper part of the collection tube. Since the density of aqua ammonia is less than that of water, it was very convenient to be able to lead the fresh water to the upper surface of the absorbing column The collected gas could also be transferred into the drying system G and the density of a sample determined by removing and weighing the bulb H. Liquid or solid products were examined after the reaction tube had been removed from the system. The addition of a liquid reagent was accomplished by replacing one of the introduction tubes B with the small buret I. A two-way stopcock J permitted a gaseous reagent to be bubbled through the solutions and, when necessary, the entire system could be filled with a gas other than air or ammonia by means of the inlet K.

The Action of Ethyl Bromide on Monosodium Bemophenone.––The ketone was put in the reaction tube, which was then connected to the apparatus and evacuated. The reaction tube was then filled with ammonia gas, the ground-in fitting B removed and the sodium in the form of spherical pellets dropped into it. It was replaced at once and the apparatus again evacuated, after which the condensation of ammonia in the reaction tube was carried out. The sodium pellets were obtained by cutting the metal into small pieces, melting it under paraffin, washing with petroleum ether and weighing under "Nujol," which was removed by a second washing in petroleum ether. After a suitable quantity of ammonia had been condensed, the sodium was added by turning the fitting in its socket and tapping it gently until the pellets dropped in. They could thus be added one at a time or all at once, as desired. When the formation of the ketyl was completed and the entire line connecting the reaction tube with the collection tube thoroughly swept out with ammonia gas, the ethyl bromide was added through the buret I and the evolved gases were collected. In two experiments employing 1.82 and 1.92 g. of ketone, 0.26 and 0.25 g. of sodium and about 6 cc. of ethyl bromide only about 4 cc. of gas was collected. This might well have been hydrogen, since the ammonia had been dried with sodium, which slowly reacts with the solvent forming sodamide and hydrogen. The possibility that air dissolved in the water might be displaced from solution as the ammonia dissolved and the absorbing liquid became warm was

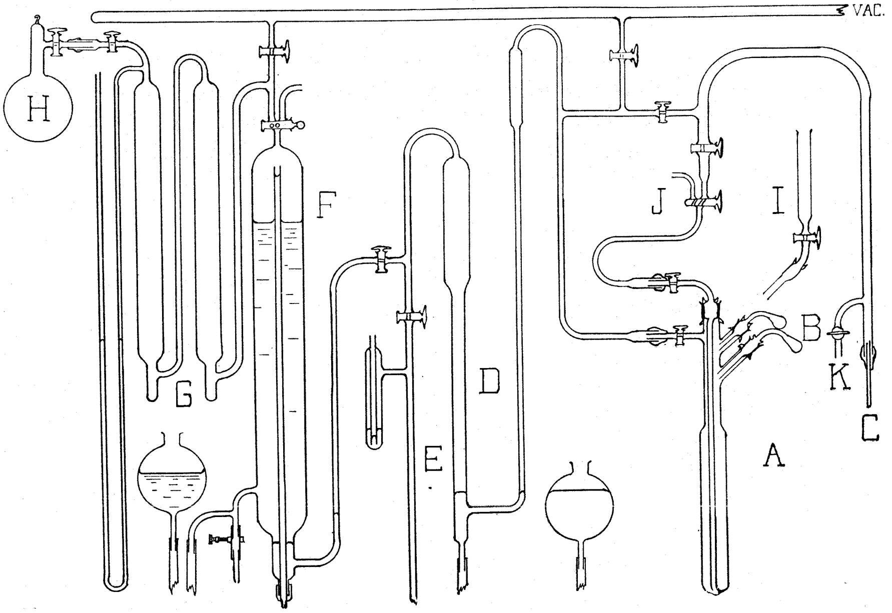


Fig. 1.—Apparatus for studying reactions in liquid ammonia.

largely eliminated by using at all times water which had been previously boiled and cooled in a closed vessel.

The non-volatile products of this reaction were examined in a previous investigation[7] and sodium bromide, benzophenone and diphenylethyl carbinol were identified, but since a quantitative separation of the organic materials was not accomplished the additional formation of gaseous products was not excluded.

The Action of Sodium on Ethyl Bromide and Benzophenone.—These experiments were carried out in a manner similar to that just described except that the ethyl bromide was added before the sodium. It dissolved the ketone and held it in solution in the presence of the liquid ammonia used. The sodium reacted vigorously with this mixture and considerable quantities of gas were evolved. In the two experiments 0.348 and 0.381 g. of sodium added to solutions containing 1.90 and 1.92 g. of ketone and about 6 cc. of ethyl bromide yielded 171 and 189 cc. of gas (under standard conditions); calcd., 170 and 186 cc. of ethane from the equation

$$C_2H_5Br + 2\,Na + NH_3 \longrightarrow NaBr + NaNH_2 + C_2H_6 \qquad (3)$$

The density of the gas was determined by collecting and weighing a dried sample in the density bulb: 339.3 cc. of gas at 24.6° and 223 mm. weighed 0.1317 g., at 25° and 239 mm., 0.1413 g.; mol. wt., 32.3, 32.4; calcd. for ethane, 30.06.

The excess ethyl bromide and ethylamine (formed from ethyl bromide and sodamide) distilled out when the ammonia was allowed to evaporate. The residue was extracted with water to remove sodium bromide and was then soluble in ether. Evaporation of the ether left a residue which was completely converted into benzophenone oxime (m. p. 140°) by treatment with hydroxylamine hydrochloride and sodium hydroxide in dilute alcohol solution. Thus it is evident that the benzophenone remained unchanged in this reaction.

The Action of Benzophenone on Disodium Benzophenone.—The disodium compound was prepared by treating the ketone with two equivalents of sodium in liquid ammonia and an equal amount of ketone was then added. The presence of a definite monosodium compound and the absence of an appreciable amount of ketone in the reaction product were demonstrated by the procedure previously employed[7] for a similar purpose.

Summary

1. It has been shown that the reaction of ethyl bromide with monosodium benzophenone in liquid ammonia is not identical with that between sodium and a solution of ethyl bromide and benzophenone in the same solvent. This fact furnishes conclusive evidence that the Schmidlin formula for the metal ketyls is incorrect.

2. It has been pointed out that the interpretation of the reactions of these compounds proposed by Schlenk and his co-workers is not necessarily the only alternative to be considered.

CAMBRIDGE, MASSACHUSETTS

---

[7] Wooster, THIS JOURNAL, 50, 1391 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

PREPARATION OF NORMAL-BUTYLMAGNESIUM BROMIDE

BY P. BORGSTROM, F. C. WAGNER AND H. C. GRIFFIN

RECEIVED JANUARY 28, 1929 PUBLISHED JUNE 5, 1929

Introduction

In the course of preparing certain compounds in fairly large amounts by means of the Grignard synthesis, it seemed of interest to make a study of the conditions giving the best yields of the Grignard reagent formed from *n*-butyl bromide, especially with a view to determining the extent to which the results of Gilman and Meyers[1] obtained with 0.05 molar quantities would hold for runs made on a large scale.

When n-butyl bromide and magnesium are brought together in ether solution, it is well known that at least three reactions may occur[2]

$$C_4H_9Br + Mg \longrightarrow C_4H_9MgBr \qquad (a)$$
$$C_4H_9MgBr + C_4H_9Br \longrightarrow MgBr_2 + \text{hydrocarbons} \qquad (b)$$
$$C_4H_9Br + Mg + BrC_4H_9 \longrightarrow MgBr_2 + \text{hydrocarbons} \qquad (c)$$

It is the conditions favoring the first of these reactions and minimizing the other two which are of interest in securing as high yields as possible of the Grignard reagent.

Materials, Apparatus and Procedures

The n-butyl bromide used was prepared from n-butyl alcohol (b. p. 117.2–117.5°) by the hydrobromic–sulfuric acid method,[3] and had a boiling point of 101.2–101.5°. An average of 300 cc. of absolute ether per mole of n-butyl bromide was used in each run. The magnesium was in the form of moderately fine turnings.

All of the runs, except No. 5 for which a 12-liter flask was used, were made in 5-liter, three-necked flasks fitted with stirrer, reflux condenser and dropping funnel. The top of the flask was packed in ice during all of the runs. By this means cooling the contents of the flask by an ice-water bath to prevent too rapid refluxing was avoided, except for brief periods in one or two of the fastest runs. Usually no refluxing occurred.

Samples for analysis were taken at the end of each run (except 14–17) by means of sampling tubes having a capacity of about 5 cc. A weighed sample was taken at the completion of Runs 14–17 by means of a thin-walled sampling bulb, and the weight of the whole contents of the flask was determined; the weight of the bromide added being known, the percentage recovery of bromide could be calculated. The analysis of the sample taken with the sampling tubes determined only the amount of bromide which had reacted, called in the tables "Recovered Br." Samples were taken after the addition of each mole of butyl bromide in Runs 6 and 17 in order to follow the course of the reaction.

Analysis for the amount of Grignard reagent present was by the acid titration method,' using $N/5$ nitric acid and $N/10$ sodium hydroxide. Some of the analyses for

---

[1] Giman and Meyers, THIS JOURNAL, 45,159,2462 (1923).

[2] For a discussion of the side reactions occurring and their possible mechanism see Gilman and Fothergill, *ibid.*, 50, 3334 (1928).

[3] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 5.

[4] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923).

bromide were made by the Volhard method, while others were done gravimetrically; both methods were used in several cases as checks.

The experimental results are given in Tables I and II.

TABLE I

FINAL RESULTS FROM SIXTEEN RUNS IN THE PREPARATION OF *n*-BUTYLMAGNESIUM BROMIDE

Run	Moles BuBr	At. wts. of Mg	Time per mole. minutes	Grignard on basis of Br recov. OH:Br recov., %	Run	Moles BuBr	At. wts. of Mg	Time per mole, minutes	Grignard on basis of Br recov. OH:Br recov., %
1	6	6	20	85.8	10	6	6.5	40	95.0
2	6	6	20	85.3	11	6	6.5	40	95.0
3	5	5	24	84.8	12	6	6.5	52	95.6
4	7	7	26	85.1	13	6	6	45	95.6
5	10	10.5	24	90.9	14	4.5	5	18	87.5
7	6	6	20	68.5	15	4.5	5	48	94.9
8	2	2	45	91.6	16	6	6.5	48	93.4
9	5.5	6	49	93.1	17	6	6.5	57	94.5

The percentages of Grignard reagent formed on the basis of bromide used were determined for Runs 14–17 as follows: Run 14, 87.6; Run 15, 93.9; Run 16, 91.7; Run 17, 91.9. The percentages of bromide recovered in these runs were: Run 14, 100.1; Run 15, 98.9; Run 16, 98.2; Run 17, 97.0.

TABLE II

INTERMEDIATE AND FINAL RESULTS FROM TWO RUNS IN THE PREPARATION OF *n*-BUTYLMAGNESIUM BROMIDE

BuBr, moles	1 Mole added in, minutes	Start to taking of sample, hr., min.	% Grig. on basis of Br rec. OH:Br recov.	BuBr moles	1 Mole added in, minutes	Start to taking of sample, hr., min.	% Grig. on basis of Br rec. OH:Br recov.
Run 6;	6 **atomic weights of magnesium**			**6a**	..	18–30	84.0
1	30	1–0	85.5	6b	..	69–30	83.90
a	..	1–30	91.9	**Run** 17;	6.5 **atomic weights of magnesium**		
2	30	2–15	90.4	2	83	2–45	90.1
3	8	3-0	87.0	3	55	3–40	92.9
4	27	3-45	87.4	4	50	4–30	93.6
5	12	4-30	87.3	5	40	5–10	95.2
6	33	5-20	87.1	6	25	5–35	94.5

Discussion of Results

Rate of Addition of Butyl Bromide.—Runs 1–4, in which the rate of addition of the bromide did not vary markedly, agree closely in their yields of Grignard reagent. Run 4 developed marked turbulence after the addition of the fourth mole, though the rate of addition was slightly slower than in any previous run. No explanation of this which seemed adequate could be formulated. It was, however, a somewhat larger run than those preceding, so the amounts used in Run 5 were larger still, the object being to determine whether a large amount of magnesium present in the early stages of the reaction had a definite accelerating effect and whether runs on a ten-mole scale could be made satisfactorily. The run proved to be a quiet one with a markedly increased yield. The quantities of materials used were not employed again as the large amounts were unsatisfactory in further manipulations. The increased yield led to the procedure adopted for Run 6, in which a sample was taken after the addition of each mole of butyl bromide in order to find out the quantities of Grignard reagent present in successive stages of the reaction. The results, shown in Table II, were disappointing in that, through accident, the rates of addition of the third and fifth moles were so much greater than the thirty-minute rate desired. The marked drop in the OH:Br ratio after the addition of the third mole in place of the rise shown in Run 17 shows very plainly the bad results obtained by adding the alkyl halide too rapidly.

Runs 8–17 show, with the exception of Number 14, a reasonable uniformity of yield; it will be noted that the molar rate of addition was in every case forty minutes or more and that no marked gain in yield is secured by any increase over this time—a complete verification of the conclusions of Gilman and Meyers. Further evidence might be found in the results of Run 17, in which a progressively decreasing time of addition of each successive mole of butyl bromide was used, finally getting, for the sixth mole, below the forty-minute limit, with resultant decrease in the OH:Br ratio. Run 14 was intentionally made at a rapid rate as a final confirmation of the lowered yield to be expected from increased rate of addition.

Reverse Process of Addition.—Run 7 was carried out with the suspicion—amply justified by the results—of poor yields to be obtained by adding magnesium to the alkyl halide, since by this procedure the latter is present in excess throughout the reaction. The completeness with which the results of this run justified the suspicions entertained may be seen from the figure for percentage yield given in Table I.

Excess of Butyl Bromide.—A consideration of the reactions given in an introductory paragraph will afford an explanation of why an unduly high concentration of butyl bromide results, as has been found always to be the case, in reduced yields of Grignard reagent. Any reaction, such as b and c, which uses up butyl bromide while producing no butylmagnesium bromide, obviously reduces the amount of the latter which can be secured from a given amount of the former by Reaction a. To the fact that a slow addition rate of butyl bromide to magnesium keeps the concentration of butyl bromide at a minimum may be ascribed the high yields obtained by this method of operation. The drop in the OH:Br ratio after the addition of the third mole in Run 6 shows the bad effect of an excess of butyl bromide, brought about by its introduction at a rate greater than that at which it could react according to Equation a, and reacting instead according to one or both of Equations b and c. The further drop of 3% in the sample taken in this run after eighteen and one-half hours further indicates that this same factor is at work. Sample 6 had been taken in the evening after only fifteen minutes' stirring subsequent to the addition of the sixth mole. When the stirrer was started the next morning enough heat was spontaneously developed to cause active refluxing, indicating the presence of unchanged butyl bromide which further stirring had caused to react, chiefly again according to one or both of Reactions b and c. It might be noted in passing that analyses made on this run on further standing show that the reaction was completed at this time and also point to the permanence of the Grignard reagent, already noted by others.[5] The very low yield obtained in Run 7 has already been given as essentially due to the constant presence of an excess of butyl bromide throughout the reaction. Just what amount constitutes an "excess" is not known; it has been repeatedly found, however, that when the ratio of the amount of free alkyl halide to the amount of active magnesium present in the reaction mixture exceeds a certain definite small value, low yields of Grignard reagent are obtained. In practice the value of this ratio is kept low by the slow addition of the alkyl halide. What has been said previously about the effects of the rate at which the butyl bromide is added and of the reverse process of addition are essentially corollaries of the effect of the presence of excess of butyl bromide.

Excess of Magnesium.—Comparison of results from Runs 8–17 shows no advantage in the half-mole excess of magnesium present in most of the runs, the highest yields (Runs 12 and 13) being obtained one with it and one without. It was used in most of the runs to make sure that the necessary slight excess would always be present. Equimolecular proportions of alkyl halide and magnesium will usually insure a sufficient excess, as pointed out by the investigators previously mentioned.

Yields.—An average of the percentage yields of Grignard reagent from the runs from which good yields could be expected (8–13, 15–17) gives 94.3% on the basis of the n-butyl bromide taking part in the reaction, or "recovered." An average of the yields based on the whole amount of n-butyl bromide used gives 92.5% for Runs 15–17 (the figure for Run 14 is omitted as being somewhat anomalous); while the average for the same runs on the basis of bromide recovered is 94.3%, which is 1.8% higher than the average based on bromide used. If this difference obtained in all the runs, the average percentage yield on the basis of bromide used would be 94.3 − 1.8 = 92.5%. This is somewhat (1.2%) higher than the figure given by Gilman and McCracken[6] as obtained with n-butyl bromide in their small quantitative runs but the agreement seems excellent

---

[5] Gilman and Meyers, *Ind. Eng. Chem.*, **15**, 61 (1923).

[6] Gilman and McCracken, THIS JOURNAL, 45, 2462 (1923).

between experiments in which the quantities of reactants in one series were usually 120 times as great as in the other.

Summary

1. A study has been made of the following conditions affecting the yield of Grignard reagent formed from n-butyl bromide: rate of addition of butyl bromide, reverse process of addition, excess of butyl bromide and excess of magnesium.

2. The yields obtained on the large scale are in close agreement with those obtained by Gilman and co-workers in quantitative work on the small scale.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

PHENOL-HALO-PHTHALEINS. PRELIMINARY PAPER[1]

BY F. F. BLICKE AND F. D. SMITH

RECEIVED JANUARY 31, 1929 PUBLISHED JUNE 5, 1929

Extensive practical use has been made of the fact that the halogens, chlorine, bromine and iodine, when introduced into certain synthetic organic compounds, greatly increase the hypnotic activity in some cases and in other instances augment the antiseptic power of the parent substance; chlorine and bromine are used especially for the former purpose, iodine for the latter.

It would be of considerable interest to know just what change could be effected by the introduction of fluorine instead of the other halogens. At present very little information is to be found in the literature regarding the physiological activity of any type of organic fluorine compounds;[2] to a large extent our lack of knowledge of these substances may be attributed to the fact that comparatively few organic fluorides have been prepared.

Phenolphthalein and various tetra-halogen substitution products have found extensive use in medicine, the former as a laxative, the latter as diagnostic agents. Fluoro derivatives of phenolphthalein have never been described. Since the effect of fluorine can be determined only by comparison of the fluoro compound with the corresponding chloro, bromo and iodo derivatives, we decided to attempt the preparation of the complete series of substances—phenol-fluoro-, -chloro-, -bromo- and -iodophthalein.

We prepared, first, five mono-halogenated phthalic acids, the 4-fluoro-,

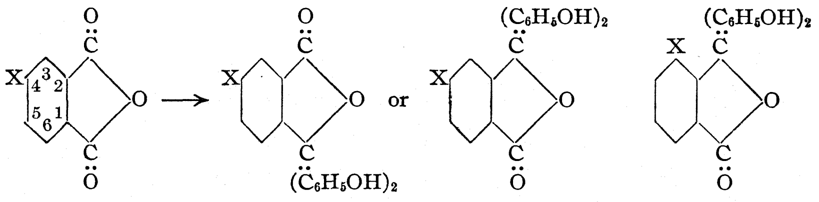
---

[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. We wish to express our appreciation for the aid which has been given us.

[2] Frankel, "Die Arzneimittel-Synthese," J. Springer, Berlin, 1927, p. 616.

4-chloro-, 4-bromo-, 4-iodo- and the 3-iodophthalic acid. After a considerable number of attempts had been made to obtain these acids from the corresponding aminophthalic acids and from the aminophthalimides by the aid of the Sandmeyer reaction, it was found, finally, that the halogenated phthalic acids could be prepared most satisfactorily from the aminodiethylphthalates. Each acid was then converted into its anhydride and the latter condensed with phenol to form the phenol-halo-phthalein.

Obviously the condensation of a 4-halophthalic anhydride with phenol may yield two isomeric phenol-halo-phthaleins, I or II, or a mixture of these compounds.



I II III

In the case of the 3-halo derivatives, likewise, two types of isomeric phthaleins are possible. Hitherto, as far as we have been able to discover, no mono-substitution products of phthalic anhydride have been condensed with phenol to form mono-substituted phthaleins. However, Stephens[3] has shown that 4-bromophthalic anhydride condenses with benzene to form a mixture of two isomeric bromobenzoylbenzoic acids; 3-bromophthalic anhydride and benzene yielded only one bromobenzoylbenzoic acid. From the condensation of benzene with 4-nitrophthalic anhydride and also with 3-nitrophthalic anhydride, Lawrance,[4] in each instance, isolated two isomeric nitrobenzoylbenzoic acids. According to Orndorff and Kline[6] benzoylbenzoic acids are intermediate products in the formation of phthaleins.

We found that all of the 4-halo-qhthalic anhydrides, when condensed with phenol, formed products which, based on halogen analysis, were pure phenol-halo-phthaleins. The products, however, showed great tendency to separate from solution in the form of oils which were very difficult to convert into a crystalline state. The crystalline material, when it was finally obtained, did not melt sharply but melted over a considerable range. 3-Iodophthalic anhydride, when condensed with phenol, was converted into a product which crystallized readily and melted sharply. These results indicate that 4-substituted phthalic anhydrides condense

---

[3] Stephens, THIS JOURNAL, 43,1950 (1921).

[4] Lawrance, *ibid.*, 42, 1871 (1920).

[5] Orndorff and Kline, *ibid.*, 46,2276 (1924).

with phenol to form a mixture of isomeric phthaleins, but in the case of the 3-substituted phthalic anhydride only one phthalein is formed."

In order to secure proof that the phthaleins obtained from the 4-halo-phthalic anhydrides were mixtures, and to determine the structure of the phthalein obtained from 3-iodophthalic anhydride, the various phenol-halo-phthalein~were fused with alkali. Baeyer[7] showed that phenolphthalein, when fused with alkali, yields *p,p'*-dihydroxybenzophenone and benzoic acid, A compound of Structure I should yield, accordingly, a m-halo-benzoic acid, or a *m*-hydroxybenzoic acid if the halogen were removed during the fusion, and *p,p'*-dihydroxybenzophenone, while from Compound II there should be formed, in addition to the ketone, a *p*-halo- or *p*-hydroxybenzoic acid. We found that the phthaleins obtained from the condensation of a 4-halo-phthalic acid and phenol yielded upon fusion with alkali small amounts of *p,p'*-dihydroxybenzophenone and a mixture of *m*- and p-hydroxybenzoic acids; the acids were separated in the form of their p-nitrobenzyl ester-ethers.[8] Prom the alkali fusion of the phthalein prepared from 3-iodophthalic anhydride and phenol there was obtained only *m*-hydroxybenzoic acid. It appears, therefore, that condensations of 4-halo-phthalic anhydrides with phenol yield mixtures of phthaleins of the type I and II, while a 3-halo-phthalic anhydride condenses with phenol to form only one phthalein, a substance of Type III.

Several questions arose in connection with the alkali fusions. Is the decomposition into dihydroxybenzophenone and substituted benzoic acid quantitative and are these fusion products stable under the conditions to which they are subjected during the fusion? The first question should be answered, we believe, in the affirmative. From the fusion of phenolphthalein with potassium hydroxide results were obtained which indicate that the initial fusion is probably quantitative. *p,p'*-Dihydroxybenzophenone, however, as Baeyer has shown,[9] is converted into phenol and carbon dioxide by vigorous fusion with alkali. Since a more prolonged alkali treatment was required to decompose the phenol-halo-phthaleins than was necessary for phenolphthalein, it is not surprising that phenol and only small yields of dihydroxybenzophenone were obtained from the fusion of phenol-halo-phthaleins. It was shown by experiment that under the conditions used in our fusions dihydroxybenzophenone was decomposed to a considerable extent but no p-hydroxybenzoic acid resulted

---

[6] We had hoped to obtain further evidence to support this view by a study of the interaction of 3-fluoro-, 3-chloro- and 3-brornophthalic anhydride with phenol. However, due to certain circumstances, these condensations could not be studied at this time. It is our intention to investigate these reactions and to prepare, also, a series of halo-phenolphthaleins.

[7] Baeyer, *Ann.*, **202**, 127 (1880).

[8] Blicke and Smith, THIS JOURNAL, **51**, 1558 (1929).

[9] Baeyer, *Ann.*, **202**, 129 (1880).

as a decomposition product; *p*-hydroxybenzoic acid, under the same conditions, remained unchanged. *p*-Bromobenzoic acid was converted practically quantitatively into p-hydroxybenzoic acid.

Experimental Part

4-Aminodiethylphthalate.—Phthalic anhydride was nitrated,[10] with the formation of 3- and 4-nitrophthalic acids. After nitration had been effected the reaction mixture was poured into 300 cc. of water. Twenty-four hours later the nitro acids, which had precipitated completely, were filtered through a Jena filter and washed with a small amount of concd. hydrochloric acid in order to remove nitric and sulfuric acids. It was found that the nitrophthalic acids which are very soluble in water are only moderately soluble in concd. hydrochloric acid. The nitro acids were dried thoroughly and then suspended in an amount of absolute alcohol equal to one and one-half times the weight of the nitro acids. After the mixture had been partially saturated with hydrogen chloride, it was refluxed for twenty-four hours. The greater part of the alcohol was removed under diminished pressure and the residue was poured into three times its volume of water. The oily ester layer, which consisted of a mixture of the diethyl ester of 4-nitrophthalic acid and the mono-ethyl ester of 3-nitrophthalic acid, was washed thoroughly with small amounts of water and then treated with 10% sodium carbonate solution. The former compound remained undissolved while the latter passed into solution in the form of the sodium salt.[11] After separation of the insoluble diethyl ester of 4-nitrophthalic acid, it was dried over fused sodium sulfate and fractionated under diminished pressure. The portion which boiled at 210–213° under 21-mm. pressure, a light yellow, viscous oil, was dissolved in an equal volume of absolute alcohol and cooled with ice. After some time the ester separated in crystalline form. The material was filtered quickly through a Büchner funnel which had been cooled previously to 0°. Unless the mixture of ester and alcohol is kept cold, the ester redissolves in the solvent. The crystalline ester was suspended in a small amount of absolute alcohol, cooled to 0° for a short time and filtered again. The compound was then obtained in the form of colorless crystals; m. p. 33–34°.[12]

In order to prepare 4-aminodiethylphthalate, 26 7 g. of the 4-nitrophthalic ester was dissolved in 100 cc. of absolute alcohol and reduced with hydrogen in the presence of 0.1 g. of platinum oxide catalyst,[13] under an initial pressure of 4 atmospheres. The reduction was complete in twenty minutes; some heat was evolved during the reaction. The catalyst was used for several reductions without reactivation with air and showed only a slight decrease in activity. The colorless or slightly yellow alcoholic solution was filtered and the filtrate concentrated on a steam-bath. After the oily residue had been cooled the amino ester was obtained in the form of colorless crystals which melted at 97–98' after recrystallization from alcohol. The melting point of this substance recorded in the literature[14] is 95°. The yield was 21.5 g. or 92% of the calculated amount.

4-Fluorodiethylphthalate.—Eleven and eight-tenths g. of 4-aminodiethylphthalate was dissolved in a mixture of 20 cc. of concd. hydrochloric acid and 10 cc. of water, the solution was cooled to 0° and then diazotized with 3 5 g. of sodium nitrite dissolved in 15 cc. of water. To the cold, diazotized solution there was added a solution of hydro-

---

[10] Littmann, THIS JOURNAL, 47,1980 (1925).

[11] Miller, *Ann.*, 208,227 (1881).

[12] Miller, *ibid.*, 208,227, 234 (1881).

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

[14] Miller, *Ann.*, 208,237 (1881).

borofluoric acid. The latter had been prepared previously by the addition of 9.2 g. of pure boric acid to 21.8 cc. of pure 48% hydrofluoric acid in a bakelite beaker. The mixture was stirred rapidly, whereupon the diazonium borofluoride of diethylphthalate precipitated in crystalline form.[15] The latter was filtered and washed with absolute alcohol and then absolute ether. The diazonium compound was dried in a vacuum desiccator over sulfuric acid for twenty-four hours. The yield was 16.5 g. or 98% of the calculated amount. The compound decomposes at 125° with the evolution of nitrogen and boron fluoride.

Ten g. of the dry diazonium compound was placed in a 500-cc. round-bottomed flask connected to a wash bottle which contained a 10% solution of sodium hydroxide. The flask was heated slowly to 125° in an oil-bath and when the evolution of gases had abated the temperature of the bath was raised to 140° and maintained there for one hour. The oily residue was dissolved in carbon tetrachloride, the solution washed with 10% aqueous sodium hydroxide, separated and dried over fused sodium sulfate. The solvent was removed and the residue distilled. There were obtained 3.5 g of a product which boiled at 165–170° under 25 mm. pressure and 2.5 g. of material which boiled at 200–250°. The lower-boiling portion was 4-fluorodiethylphthalate; the yield corresponded to 50% of the calculated amount.

4-Fluorophthalic Acid.—Twenty-one g. of the fluoro ester was added to 20 g. of sodium hydroxide dissolved in 50 cc. of 50% alcohol. The mixture was then refluxed for three hours, the alcohol removed and the solution acidified with sulfuric acid; the fluorophthalic acid was extracted with ether, the solvent removed and the oily residue allowed to crystallize. After recrystallization from acetic acid the acid melts at 147–148° in a sealed tube. It is very soluble in water, acetic acid and ether.

4-Chlorodiethylphthalate.—Eleven and eight-tenths g. of 4-aminodiethylphthalate was dissolved in a mixture of 20 cc. of concd. hydrochloric acid and 10 cc. of water and diazotized with 3.5 g. of sodium nitrite dissolved in 15 cc. of water. Cuprous chloride had been prepared previously from 21 g. of copper sulfate, 5.4 g. of sodium chloride, 4.4 g. of sodium bisulfite and 3 g. of sodium hydroxide.[16] The cuprous chloride was suspended in a mixture of 100 cc. of water and 25 cc. of concd. hydrochloric acid. The diazotized solution was introduced slowly and with rapid stirring below the surface of the suspension of cuprous chloride. The mixture was then heated on a steam-bath for some time. The oily layer was extracted with carbon tetrachloride, the solution washed with dilute hydrochloric acid and then dried over fused sodium sulfate. The solvent was removed and the residue distilled. The greater portion of the material boiled at 185–190° under 25 mm. pressure.[17] The yield was 9 g. or 70% of the calculated amount.

4-Chlorophthalic Acid.—Thirty-five g. of 4-chlorodiethylphthalate was hydrolyzed with 30 g of sodium hydroxide which had been dissolved in 60 cc. of 50% alcohol. The chloro acid, after recrystallization from acetic acid, melted at 150° in a sealed tube[18] The acid is soluble in water, ether and acetic acid.

4-Bromodiethylphthalate.[19]—Eleven and eight-tenths g. of the 4-amino ester was

---

[15] The preparation of nuclear fluorine compounds by means of diazonium borofluorides has been patented by Bart (German Patent 281,055) and has been used by Wilke-Dorfurt and Balz, Ber., 60, 115 (1927); Balz and Schiemann, *ibid.*, 60, 1186 (1927), and by Schiemann and Bolstad, *ibid.*, 61, 1403 (1928).

[16] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33.

[17] Rée, *Ann.*, 233, 238 (1886), states that the substance, prepared by esterification of 4-chlorophthalic acid with ethyl alcohol, boils at 300–305° under ordinary pressure.

[18] Egerer and Meyer, *Monatsh*, 34, 81 (1913), record the melting point as 150°.

[19] 4-Bromodiethylphthalate has been prepared by Faust, Ann., 160, 64 (1871), by esterification of the acid.

dissolved in a mixture of 20 cc. of 48% hydrobromic acid and 10 cc. of water and was then diazotized with 3.5 g of sodium nitrite dissolved in 15 cc. of water. Cuprous bromide was suspended in 100 cc. of water and 15 cc. of 48% hydrobromic acid and the diazotized solution introduced slowly below the surface of the suspension with rapid stirring. The cuprous bromide had been prepared from 10.5 g of copper sulfate, 5 5 g. of sodium bromide, 2.2 g. of sodium bisulfite and 1.5 g. of sodium hydroxide [20] The mixture was heated on a steam-bath and the oily layer was extracted with carbon tetrachloride. The carbon tetrachloride solution was washed with dilute hydrochloric acid, dried over fused sodium sulfate and the solvent removed From the residue there was obtained 11 g. of material which boiled at 225° under 60-mm. pressure. The yield is 70% of the calculated amount.

4-Bromophthalic Acid.—Forty-two g. of the above ester was hydrolyzed with 30 g. of sodium hydroxide and 100 cc. of 50% alcohol. The bromo acid was recrystallized from acetic acid; m. p. 170° in a sealed tube. Stephens[21] found 170.5" as the melting point.[22]

4-Iododiethylphthalate.—Eleven and eight-tenths g. of 4-aminodiethylphthalate was dissolved in a mixture of 20 cc. of concd. hydrochloric acid and 10 cc. of water and diazotized with 3.5 g. of sodium nitrite dissolved in 15 cc. of water. The diazotized solution was treated with 12 g. of potassium iodide in 100 cc of water. The iodo ester was obtained in the form of a red oil [23]

4-Iodophthalic Acid.—Thirty-two g. of iodo ester was hydrolyzed with 25 g. of sodium hydroxide in 75 cc. of 50% alcohol. The crude acid was dissolved in water and boiled with charcoal. After filtration the filtrate was concentrated to a small volume. The iodo acid was recrystallized from acetic acid; m. p. 185–186° in a sealed tube. Edinger[23] found 182°. The yield based on the iododiethylphthalate was 59% of the calculated amount. The acid is soluble in water, ether and acetic acid.

3-Aminodiethylphthalate.—The solution of the sodium salt of the motlo-ethyl ester of 3-nitrophthalic acid was acidified with hydrochloric acid. Most of the acid ester was precipitated in the form of an oil, which was separated from the aqueous layer and then washed several times with small amounts of water. The acid ester was converted into the ammonium salt and precipitated as the silver salt with silver nitrate.[24] The silver salt was thoroughly dried, suspended in benzene and then refluxed with an excess of ethyl bromide for eight hours.[25] The silver bromide was filtered and the benzene removed on a steam-bath. The oily residue was dissolved in absolute alcohol and the ester reduced with hydrogen and platinum oxide catalyst. The amount of ester obtained from 0.1 mole of silver salt was reduced with hydrogen under an initial pressure of 4 atmospheres in the presence of 0.1 *g.* of catalyst. After ten minutes no more

---

[20] This preparation of cuprous bromide is entirely analogous to the preparation of cuprous chloride given in "Organic Syntheses," except that sodium bromide was used instead of sodium chloride.

[21] Stephens, THIS JOURNAL, 43, 1952 (1921).

[22] At the time this investigation was finished, Baker published a note, J. Cham. *Soc.*, 2829 (1928), stating that he had prepared *p*-bromophthalic acid from 4-nitrodiethylphthalate. The latter substance was reduced by means of zinc and hydrochloric acid, the amino compound was converted into the bromo derivative by the aid of the Sandmeyer reaction and the bromo ester finally hydrolyzed by barium hydroxide. The melting point of 4-bromophthalic acid was recorded as 173–175°.

[23] Edinger, J. *prakt. Chem.*, [2] 53,386 (1896).

[24] Miller, *Ann.*, 208, 244 (1881).

[25] The diethyl ester of 3-nitrophthalic acid has been prepared by Miller[24] from the di-silver salt of 3-nitrophthalic acid and ethyl iodide.

hydrogen seemed to be absorbed. The alcohol was then removed and the 3-aminodiethylphthalate obtained in the form of an oil.[26] The amount of hydrogen absorbed indicated the presence of 0.07 mole of 3-aminodiethylphthalate.

3-Iododiethylphthalate.—The oily residue obtained from the previous experiment was treated with 20 cc of concd. hydrochloric acid and 10 cc. of water and then diazotized. The diazotized solution was introduced slowly, with rapid stirring, below the surface of a solution prepared from 12 g. of potassium iodide and 100 cc. of water. The oily layer which formed was decolorized by the addition of sodium bisulfite and then cooled. The crystalline material which formed melted at 70°.[23] The yield, based on the silver salt of the mono-ethyl ester of 3-nitrophthalic acid, was 40% of rhe caicuiated amount.

3-Iodophthalic Acid.—3-Iododiethylphthalate was hydrolyzed with alcoholic sodium hydroxide.[23] The alkaline solution was acidified with sulfuric acid, the organic acid extracted with ether, the ether layer separated and the solvent removed. The residue was dissolved in water and the solution boiled with charcoal. After filtration and concentration of the filtrate, the 3-iodophthalic acid separated in crystalline form; m. p. 206°. The compound is soluble in water, ether and acetic acid.

The acid was prepared by a second method. 3-Nitrophthalic acid was reduced with stannous chloride and hydrochloric acid.[27] The hydrochloride of the amino acid which formed was filtered, suspended in dilute hydrochloric acid, diazotized and then treated with potassium iodide.

TABLE I

HALO-PHTHALIC ANHYDRIDES

			Analyses (Volhard)			
Anhydride	**B. p., °C.**	**M. p., °C.**	**Calcd. for** $C_8H_3O_3X$		**Found**	
4-Fluoro[a]	260 (746 mm.)	76–78	F[b]	1147	11.08	11.12
4-Chloro"	284[c] (750 mm.)	98	Cl	1945	19.30	19.30
4-Bromo[a]	290–293 (750 mm.)	108–109[d]	Br	35.20	35.10	35.18
4-Iodo[e]	......	125–126	I	46 32	46.32	
3-Iodo[e]	......	159–161	I	46.32	46.28	46.31

[a] Prepared by heating the acid until all of the water formed through the conversion of the acid into the anhydride had been removed. The residue was then distilled. The distillate solidified immediately; it was recrystallized from acetic anhydride.

[b] Starck, *Z. anorg. Chem.*, 70, 173 (1911).

[c] Egerer and Meyer, *Monatsh.*, 34, 81 (1913), state that the anhydride boils at 297° and melts at 98°.

[d] Stephens, ref. 3, states that the compound melts at 104106".

[e] Prepared by heating the acid for ten minutes with an equal weight of acetic anhydride. The iodo-anhydride separated when the solution was cooled. The material was recrystallized from acetic anhydride and washed with absolute ether.

Phenol-halo-phthaleins

Preparation.—Five-hundredths mole of the halo-phthalic anhydride, 0.10 mole of freshly distilled phenol and 0.10 mole of fused zinc chloride were heated by means of an oil-bath at 115–130° for twenty-four hours. An additional quantity of phenol, 0.10 mole, was added and the mixture heated for twenty-four hours longer.

The reaction mixture was treated with 20 cc. of concentrated hydrochloric acid and 10 cc. of water and steam distilled for one hour. The hot supernatant liquid was de-

---

[26] Miller, *Ann.*, 208,246 (1881).

[27] Bogert and Jouard, THIS JOURNAL, 31,484 (1909).

canted from the oily residue and the latter again steam distilled for one hour. The combined supernatant liquors were cooled and extracted with ether. The ether layer was washed with dilute hydrochloric acid, the solvent removed and the residue dissolved in water, filtered and the filtrate evaporated to dryness. The residue was unchanged halo-phthalic acid. The oily water-insoluble residue from the steam distillation solidified to a resinous mass when cooled. The latter was pulverized, extracted with 10% sodium hydroxide, filtered and the filtrate acidified with dilute hydrochloric acid, whereupon the phenol-halo-phthalein was precipitated. There was obtained a small amount of alkali-insoluble material, which was probably a halo-fluoran.

The crude phthalein was filtered, washed with water and dissolved in **100** cc. of methyl alcohol; then **40** cc. of water and 2 g. of charcoal were added and the mixture refluxed for three hours. The hot solution was filtered and the solvent allowed to evaporate slowly. **A** gum was obtained, which was dissolved in 10% sodium hydroxide, filtered, the filtrate diluted to **500** cc. and the phthalein precipitated with dilute hydrochloric acid. The precipitate was filtered, washed well and air dried. The substance obtained was electrostatic and was very soluble in practically all organic solvents; it had no definite melting point. The resinous material was dissolved in acetic acid. After several days the crystalline material which had deposited was recrystallized from acetic acid. The amount of alkali-insoluble material from the several halo-phthalic anhydrides varied from 0.05–1.3 g The amorphous phthaleins were very soluble in all organic solvents but after conversion into the crystalline state they were found to be very insoluble except in hot acetic acid. In the case of 3-iodophthalic anhydride the reaction product became granular during the steam distillation. The granular material was recrystallized from dilute methyl alcohol and then from acetic acid.

TABLE II

3- AND 4-HALO-PHTHALIC ANHYDRIDES AND PHENOL

Anhydride	Yield of alkali-soluble material[a] (halo-phenol phthalein), %	M. p. of crystalline material, °C.	Analyses (Volhard), % Calcd. for $C_{20}H_{13}O_4X$		Found	
4-Fluoro	54	230–240	F[b]	5.65	5.34	5.42
4-Chloro	76	214–233	Cl	10.05	9.86	9.93
4-Bromo	73	226–236	Br	20.15	20.20	20.00
4-Iodo	63	240–255	I	28.58	28.68	28.30
3-Iodo	45	252–254	I	28.58	28.70	28.80

[a] Based on the halo-phthalic anhydride.

[b] Starck, *Z. anorg. Chem.*, **70, 173** (1911).

Alkali Fusions

Two g. of phenolphthalein was fused with 10 g. of potassium hydroxide[28] and 1-2 cc. of water in a nickel crucible until the color of the reaction mixture had changed to a light yellow. It was not necessary to fuse the material longer than three to four minutes to effect this change. The fusion mixture was dissolved in **75** cc. of water and acidified with dilute sulfuric acid, whereupon *p,p'*-dihydroxybenzophenone and benzoic acid precipitated. After the mixture had cooled the crystalline material was filtered and the latter treated with dilute ammonium hydroxide until the solution was alkaline to phenolphthalein. The ammoniacal solution was extracted twice with 25-cc. portions of ether. Upon evaporation of the solvent there was obtained almost pure *p,p'*-dihydroxybenzophenone; after recrystallization from water the material melted at 212–213°.[29]

---

[28] Baeyer, **Ann., 202,** 127 **(1880).**

[29] Montagne, *Rec. trav. chim.*, **39,348** (1920).

The yield was 1.15 g. which is 80% of the calculated amount. The aqueous alkaline layer from the ether extraction was acidified and the precipitated benzoic acid filtered. The latter weighed 0.59 g or 73% of the calculated amount; m. p. 121°. More benzoic acid remained dissolved in the filtrate but through an oversight this was not isolated.

One g. of *p,p'*-dihydroxybenzophenone was fused with 10 g. of potassium hydroxide for ten minutes at 200–250°. Sixty per cent. of the material was recovered unchanged, the remainder having been converted into phenol and carbon dioxide." No *p*-hydroxybenzoic acid was obtained.

One g. of *p*-bromobenzoic acid was fused with 10 g of potassium hydroxide for ten minutes at 200–250°. The fusion mixture was dissolved in water, acidified and extracted with ether. From the ether layer there was obtained p-hydroxybenzoic acid; m. p. 208–210°.[31]

One g. of p-hydroxybenzoic acid was fused with 10 g. of potassium hydroxide for ten minutes at 200–250°. Ninety-five per cent. of the acid was recovered; m. p. 210–211°.

Phthalein from 4-Fluorophthalic Anhydride.—Two g. of the phthalein was fused with 8 g. of potassium hydroxide and 1–2 cc. of water at 200–250°. The fusion mixture was dissolved in 50 cc. of water, acidified with dilute sulfuric acid, cooled and the *p,p'*-dihydroxybenzophenone which had precipitated was filtered off. It weighed 0.5 g. or 39% of the calculated amount; m. p. 208–210°. The aqueous, acidic filtrate was extracted with ether. After removal of the solvent the residue was dissolved in water, boiled with charcoal, filtered and the filtrate evaporated to dryness. There was obtained 0.8 g. of a mixture of m- and p-hydroxybenzoic acids; the yield corresponds to 97% of the calculated amount.

The general procedure used to separate the mixture of hydroxybenzoic acids obtained from the alkali fusions was as follows. The mixture of acids and one molecular equivalent of potassium carbonate were dissolved in 5 cc. of water. This solution was added to 2.1 molecular equivalents of p-nitrobenzyl bromide dissolved in 15 cc. of pure acetone. The mixture was refluxed for two hours, cooled and the crystalline material filtered. The latter was treated with cold, dilute sodium hydroxide and the undissolved portion recrystallized from acetone. The dinitrobenzyl derivative of the para acid8 is practically insoluble in hot acetone while the meta derivative is much more soluble in this solvent; a practically complete separation of the two derivatives can be effected by two recrystallizations from acetone. The yield of the di-nitrobenzyl derivative of the *p*-hydroxy acid was about twice that of the meta compound. The melting point of the former substance was 196–198°, mixed melting point, unchanged. The melting point of the meta derivative was 140–143°, mixed melting point, 138–141°.

Phthalein from 4-Chlorophthalic Anhydride.—From the fusion of 2.0 g. of the phthalein there were obtained 0.7 g. of a mixture of m- and p-hydroxybenzoic acids and 0.6 g. of *p,p'*-dihydroxybenzophenone; the mixture of acids melted from 160–190". The yield of the ketone was 50% and that of the acids 91% of the calculated amount. The mixture of acids was treated as outlined previously and the same relative amounts of each derivative were obtained as in the case of the phthalein from 4-fluorophthalic anhydride. The melting point of the di-nitrobenzyl derivative of the para acid was 195–197°; that of the meta isomer, 138–141°.

Phthalein from 4-Bromophthalic Anhydride.—From the alkali fusion there were obtained a 63% yield of *p,p'*-dihydroxybenzophenone and a 92% yield of a mixture of m- and p-hydroxybenzoic acids; the mixture of acids melted from 165–195". The acids were separated and identified after they had been converted into their *p*-nitrobenzyl derivatives.

---

[30] Baeyer, *Ann.*, 202,127 (1880).

[31] Fischer, *ibid.*, 127, 145 (1863).

Phthalein from **4-Iodophthalic** Anhydride.—In this instance there were obtained from the alkali fusion only a small amount of *p,p'*-dihydroxybenzophenone and an 86% yield of a mixture of m- and *p*-hydroxybenzoic acids; the mixture melted from 165–190°.

Phthalein from 3-Iodophthalic Anhydride.—From the alkali fusion there was isolated a small amount of *p,p'*-dihydroxybenzophenone; however, m-hydroxybenzoic acid, which melted from 190–195° was obtained in a 89% yield. The hydroxy acid was further identified by conversion into the *p*-nitrobenzyl ester ether; the latter melted from 135–140° and a mixed melting point with the pure ether ester was unchanged.

The following crystallographic data have been determined by Dr. C. B. Slawson. These measurements were made upon crystals formed by the slow evaporation at room temperature of acetic anhydride solutions.

4-Fluorophthalic Anhydride.—Crystals of this compound consist almost invariably of pseudo-hexagonal twins. The twins consist of interpenetrating triclinic needles, at an angle of 8°, resembling at the terminations twinned augite crystals, though the front pinacoid is not present. The prism angle is 51°55'. The reentrant terminal angle is about 60° and the terminal faces are very poorly developed. The reentrant angle in the prism zone is about 8"; $\alpha = 1.400$; $\beta\gamma = 1.74$; 2V = 3–5"; optically negative with very pronounced $r > v$ dispersion. Extinction (following the augite analogy) is nearly parallel on 100 and —38" on 010. Bxa is very commonly observed on crushed fragments.

4-Chlorophthalic Anhydride.—This compound forms elongated triclinic needles with three pairs of faces parallel to the elongation. The measured values between these faces are 23°4', 47°46' and 109°8'. The terminations of the needles are poorly developed. $\alpha = 1.500$; $\beta = 1.700$; $\gamma = 1.775$; 2V = 55–60°; optically negative; crystals lying so that the extinction is nearly parallel to the elongation give a value close to a-perpendicular to the elongation. The extinction angles on the three faces are 3, 9 and 14°.

4-Bromophthalic Anhydride.—These crystals resemble very closely in appearance the 4-iodo crystals described below except that the prisms are 210, the clino domes are 041 and the negative orthodome is absent. The axial ratio is 1.095:1:1.091; $\beta = 59°35'$. The measured interfacial values are $210–2\bar{1}0 = 50°32'$, $\bar{1}00–\bar{1}01 = 60°9'$ and $014–0\bar{1}4 = 26°32'$. It was impossible to measure γ but a = 1.545 and $\beta = 1.700$; 2V = 90°±; optical character indeterminate; X A c + 15–16", and Z = b.

4-Iodophthalic Anhydride.—The crystals of this substance are monoclinic with an axial ratio of 1.123:1:1.139, $\beta = 73°29'$. They are elongated parallel to the *c* axis with a pronounced development of the clino-pinacoid. Other faces present are 110, 101, $\bar{1}01$ and 012. The measured interfacial angles are $110–1\bar{1}0 = 94°12'$, $101–\bar{1}01 = 89°37'$, $012–0\bar{1}2 = 57°20'$. Because of its high index of refraction it was impossible to determine γ, but $\alpha = 1.555$ and $\beta = 1.77$, 2V = 60–70°; optically negative; X very nearly *c;* and $Z = b$.

The iodo and bromo compounds are probably isomorphous. The chloro and fluoro compounds, being triclinic, may be considered either dimorphous with forms which fall in the iodo–bromo series or distinctly different. In the case of the chloro compound we have many similarities to the bromo especially in the optical properties, so the first supposition is probably correct. With the fluoro compound there is no evidence which shows such a similarity; in fact, what evidence there is seems to support the second supposition, although that cannot be definitely established from the crystallographic data.

Summary

4-Fluoro-, 4-chloro-, 4-bromo-, 4-iodo- and 3-iodophthalic anhydrides have been condensed with phenol to form phenol-halo-phthaleins. From the 4-halophthalic anhydrides, mixtures of isomeric phthaleins were obtained but in the case of 3-iodophthalic anhydride only one phthalein was found.

Data obtained by Dr. Slawson have shown that 4-fluorophthalic anhydride does not fit into the same crystallographic scheme with the three other 4-halophthalic anhydrides.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE MECHANISM OF THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. I. NORMAL OCTANE[1]

BY J. C. POPE, F. J. DYKSTRA AND GRAHAM EDGAR

RECEIVED FEBRUARY 1, 1929 PUBLISHED JUNE 5, 1929

I. Introduction

The oxidation of hydrocarbons represents a subject which has attracted the attention of many investigators, yet it cannot be said that the fundamental mechanism of such reactions has been made perfectly clear. Perhaps this has been partially due, on the one hand, to a natural tendency to generalize from results obtained on the simpler hydrocarbons and, on the other, to failure to differentiate between liquid phase reactions and vapor phase reactions.

The results of the present investigation on octanes may perhaps contribute to the interpretation of the behavior on oxidation of hydrocarbons intermediate in complexity.

No attempt will be made to give an elaborate survey of the literature on the general subject of oxidation, but a few references to vapor phase oxidation of normal paraffins may be cited. Bone[2] and his associates demon-

---

[1] Presented in part at the Fall Meeting of the American Chemical Society at Swampscott, Massachusetts, September, 1928.

[2] Bone and co-workers, *J. Chem. Soc.*, 81, 535 (1902); 83, 1074 (1903); 85, 693 (1904); 89, 660, 1614 (1906).

strated that the simpler normal hydrocarbons oxidize with the intermediate formation of aldehydes. These authors interpreted their results as indicating that an alcohol is first formed which is then rapidly oxidized to an aldehyde, a theory since well known as the hydroxylation theory. Wheeler and Blair[3] investigated the oxidation of hexane and noted the copious formation of aldehydes. A process of oxidation was formulated based on the hydroxylation theory and involving the possibility of several simultaneous points of attack on the hexane molecule.

Recently Callendar[4] has reported "acetaldehyde, formaldehyde, valeraldehyde, etc.," among the products of the vapor phase oxidation of normal hexane.

It is not possible from these data to determine by what process oxygen attacks a long carbon chain in the vapor phase and by what steps the reaction progresses.

In the present study octanes were selected for investigation because their molecular weight is about the average of commercial gasolines, the mechanism of whose oxidation is a problem of great interest. Part I presents data on the oxidation of n-octane and the oxidation of n-heptaldehyde and *n*-butyraldehyde, which were studied in order to clarify certain observations on the oxidation of n-octane; Part II will discuss the oxidation characteristics of five isomeric octanes. The reactions were studied entirely in the vapor phase, by the dynamic method.

II. Apparatus and Experimental Methods

(a) General.—Mixtures of octane vapor and air were passed through a heated glass tube and samples of the gas were taken for analysis In certain experiments the liquid products of oxidation were collected and examined. Certain details of technique seem worthy of full description. The entire apparatus is illustrated in Fig. 1.

(b) Furnace and Thermocouples.—The furnace was a tube of pyrex glass 1″ in internal diameter and about **36**" long with a reaction space of 367 cc. It was wound with resistance wire and heavily lagged with asbestos. The lagging was thicker at the ends so that in the absence of reaction the temperature was approximately constant over the entire furnace length. Temperature was controlled by external resistance. When runs were made with rising temperature, the heating current was altered by hand to keep the temperature rising smoothly. **A** run over the range of 200–650° usually occupied about two hours.

Two thermocouples were provided, one of which was inserted through either end. They could be moved to investigate the temperature gradient of the furnace but were usually placed in definite positions, one at the entrance end, *2* inches from the reaction mixture inlet (see below), the other at about 10 inches from the exit end.

(c) Method of Obtaining Combustible Mixture.—Where it is necessary to preheat the fuel for vaporization, as is the case with a high-boiling material like n-octane, it becomes essential to avoid exposure to oxygen until the proper experimental temperature

---

[3] Wheeler and Blair, J. *Soc. Chem. Ind.,* 42, 491T (1923).

[4] Callendar, Aeronautical Research Committee, London, Reports and Memoranda, No. 1062, "Dopes and Detonation," second report.

is reached. Hence the principle followed was to preheat and vaporize the fuel in nitrogen only, and to mix it as suddenly as possible with the requisite amount of oxygen when the furnace temperature had been reached.

The vaporization and mixing devices are shown in Fig. 1. The fuel was led from a 50-cc. buret reservoir to a 5-cc. buret graduated in 0.02 cc., from which it was allowed to flow at intervals into the slightly inclined arm of the feed device. The liquid head in the latter was thus maintained at any selected point by intermittent additions of small volumes. The difference in head on the shallow incline, produced by each addition, was so slight and the resistance of the capillary tube so great, that very constant rates of feed were obtained. Further, the volume fed from the small buret was read every few minutes, thus giving a continuous oversight of the fuel mixture. From the inclined arm the fuel passed through a long capillary ending in a flat ground surface within the preheater tube. Here nitrogen purified by passage through alkaline pyrogallol and dried over the calcium chloride was passed over the emerging liquid and the resulting mixture was then led to the large annular tube by which it entered the furnace. Oxygen dried over calcium chloride was led into the furnace by the inner annular tube. (The two annular tubes extended about 6 inches within the furnace heating coil.) Mixing took place in a device consisting of a glass spiral placed concentrically with the annular tubes carrying the two gases. On meeting the gases were diverted from their straight course and forced together round the spiral, in which process they became intimately mixed. The efficiency of mixing was proved by tests with oxygen and nitrogen alone, in which the gases were analyzed shortly after leaving the mixing tube.

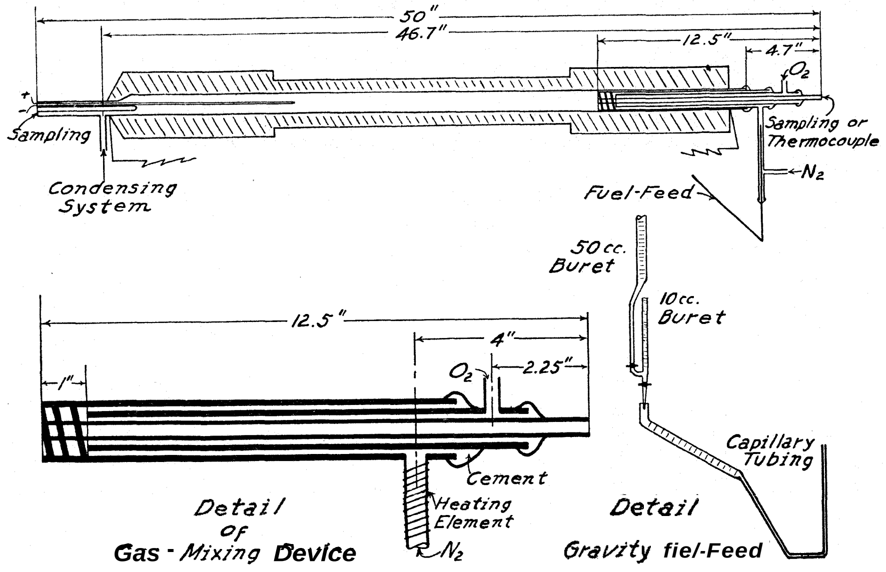


Fig. 1.

(d) Control of Mixture.—The oxygen and nitrogen were passed into the furnace at a rate identical for all experiments and were measured and controlled by flow meters. The final mixture of these gases contained about 20.5% of oxygen. The oxygen–fuel ratio was governed entirely by the amount of fuel used, and in the experiments described herein with n-octane was between 11 and **13** to 1, the theoretical ratio for octane being 12.5 to 1. These figures refer to the input of materials.

(e) Period of Contact.—The minimum time necessary for the gases to pass through the furnace was about 25 seconds at 650" and the maximum about 50 seconds at 200°. Since the reaction occurs almost entirely in a narrow zone, the actual time of reaction is less than these figures indicate.

(f) Sampling System.—Gas samples were taken over mercury. They were collected through a T-piece placed in the line beyond the condensing system, except when investigating the course of the reaction at different positions in the furnace. The samples correspond to a narrow range of temperature, when taken on a rising temperature, since the sampling occupied about ninety seconds, corresponding to a rise of furnace temperature of not over 6°. The mean sampling temperature was used as the reaction temperature of such samples.

For collecting the liquid condensate when required, four units were used, one ice-cooled glass coil, one filter cartridge to stop mist and two glass coils, cooled with carbon dioxide snow.

(g) Analytical Methods.—Gas samples were analyzed in an apparatus of the Burrell type. Analysis was made for carbon dioxide, gases absorbed by sulfuric acid, oxygen and carbon monoxide. Occasional analyses were carried through for hydrogen and methane. A blank analysis was made in each experiment of the oxygen–nitrogen mixture without fuel.

Determinations of the following constituents, acid, aldehyde, peroxide and water, were made on certain condensates from the oxidation of normal octane. The condensate was weighed, then washed from the various condensing units with water and a little alcohol, and the total volume of the solution determined. After thorough mixing, samples of known volume were taken for the determinations. Acid was determined by titration with $N/100$ sodium hydroxide, with phenolphthalein as indicator. Following the neutralization, aldehyde was determined on the same sample by the method of Ripper.[5] For the determination of peroxide, an acidified solution of potassium iodide was added to a condensate sample and the flask flushed with nitrogen, blanks (lacking only condensate sample) being treated similarly. The flasks were kept in a dark place. The titrations with $N/10$ thiosulfate were carried out in a stream of nitrogen, the addition of thiosulfate being continued until no further liberation of iodine was observed.

NOT%—It may be stated that if this determination is carried on in the presence of air, as has usually been done by previous investigators, much higher results for peroxide are obtained, caused probably by interaction of aldehydes and oxygen during the shaking A sample of pure heptaldehyde in the presence of air will give a test for peroxide, and since aldehyde and air are both present among the reaction products in the present investigation, the actual source of the peroxides found is uncertain.

For the determination of water, a separate collection of condensate was made and the liquid allowed to remain in the condensing train after weighing. The whole train was then connected to a series of gas-drying tubes containing anhydrous copper sulfate and air at room temperature was aspirated through towers of anhydrous copper sulfate and allowed to evaporate the condensate and carry it through the weighed tubes. Passage of air was continued until the weight of copper sulfate remained approximately constant.

(h) Materials Used.—The n-octane used was synthetic material with a boiling range 124.9–125 3° (763 mm., uncorr.).

The aldehydes were Eastman products, further fractionated. The boiling ranges were n-heptaldehyde, 152.1–152.6"; n-butyraldehyde 74.0–74.6° (763 mm., uncorr.).

---

[5] Ripper, Monatsh., 2, 1079 (1900).

III. Description of Results

n-Octane

(a) General.—In studying exothermic reactions of this character, where the actual temperatures of the reacting mixture may be considerably higher than the furnace temperature, and always vary at different positions in the furnace, it is somewhat of a problem to decide what temperatures are to be considered as the temperatures of reaction. Since the greater part of the reaction occurs in a short zone of the reaction tube, it was considered in this investigation that the actual temperature registered by the thermocouple in this zone was the most satisfactory basis for comparison, and these "maximum furnace temperatures" have been employed throughout in considering the effect of temperature.

Experiments were carried out in two ways: (a) at constant furnace temperature, for the purpose of examining the temperature distribution at different parts of the furnace, of collecting liquid oxidation products and of observing the extent of reaction at different positions in the furnace (for this purpose the heating current and fuel feed were held constant for a long period of time to secure equilibrium conditions before samples were taken); (b) with slowly rising temperature (about 4° per minute), gas samples being taken for analysis from time to time until any given temperature range had been covered. The mean temperature while the sample was being taken was recorded as the temperature of reaction.

As far as gaseous products were concerned the two methods gave results differing slightly quantitatively, as would be expected because of the somewhat different relationship between the temperature of the wall and that of the charge. These differences were not sufficient, however, to indicate any appreciable change in the nature of the reaction.

As will be indicated below there are certain temperature ranges in which rather abrupt changes occur in the reaction characteristics, and in these ranges it was impracticable to maintain constant temperature conditions. The phenomena observed in these temperature ranges contributed greatly to the interpretation of the reaction and the runs with rising temperature have, therefore, been selected for the detailed discussion.

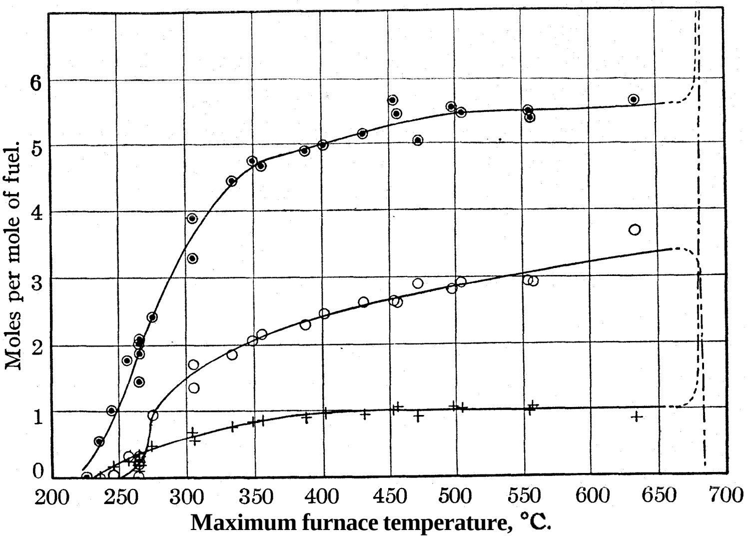
(b) Runs at Constant Temperature.—The analyses of the gaseous products of oxidation at constant temperature do not add materially to the knowledge gained from the runs at slowly rising temperature, which will be discussed fully below. They will, therefore, not be considered further, except to point out that it was clear from the results that the reaction when considerable in extent was largely localized in the first 20% of the tube length. This was shown by temperature measurements at different positions in the tube, which showed a sharp rise in temperature immediately after mixing when the reaction was proceeding to a considerable extent, and by analysis of the gaseous products, which showed little change in oxygen consumption between 20% of the tube length and the extreme end. While no corresponding measurements were made in runs with the furnace temperature rising, it seems most probable that the results would be essentially the same. A few runs at constant temperature were carried out for a sufficient length of time to collect a small portion of liquid, condensed as indicated above, from the gaseous products. These liquid oxidation products invariably contained considerable aldehyde and water. At low temperatures some unoxidized octane was recovered. Aldehyde and water were the first oxidation products detectable. Traces of peroxide (probably) were found, and at low temperatures small amounts of acid were present, diminishing as the temperature was raised and disappearing entirely at about 400°. The general nature of the oxidation products at low temperatures is shown by the following analyses at 260° (figures per mole of octane input): unoxidized octane, 0.55; aldehyde, 0.33; acid, 0.25; peroxide (?), 0.07; water, 0.36. On account of the difficulty in analyzing these small amounts of liquid and because of the possible presence of small amounts of other substances which might escape the analytical methods employed, these figures must be considered as very approximate. For these reasons the quantitative aspects of the liquid products will not be considered in the detailed discussion of the mechanism of the reaction.

(c) Runs **with** Slowly Rising Temperature.—The reactions may be divided fairly definitely into three temperature zones: 200–270°, 270–650°, above 650°, the significance of which will be discussed below. For convenience the phenomena covering the whole temperature range are described under the heads (1) oxygen consumption, (2) gaseous oxidation products and (3) luminescence. The analytical results on oxygen consumption and gaseous products are expressed graphically in Fig. 2. All data are expressed on a basis of moles per mole of octane input, and the temperatures are those recorded by the thermocouple in the center of the reaction zone. Data from five separate runs are included.

(1) Oxygen Consumption.—Below 200" no oxygen consumption is indicated by analysis. Between 200 and 270° the oxygen content of the gas decreases regularly until the consumption calculated per mole of octane amounts to about two moles. At a temperature of about 270° some alteration in the nature of the reaction is indicated by pulsations of the flow meters. The pulsations at first occur at ten to fifteen seconds apart, but gradually become more frequent and weaker until at 300–320° they are no longer noticeable. During this time there is a slightly increased rate of rise of temperature of the first thermocouple, followed by localization of the heat evolution near the thermocouple, which may then record a temperature more than 100° higher than that given by the other. Throughout this period the oxygen consumption rises steadily, but the curve gradually

becomes less steep (Fig. 2) and above 350° rises very gradually, the oxygen consumption increasing by one 1 mole from 350 to 650°, where it is nearly 6 moles. Above 650° the nature of the reaction changes again, strong pulsations are noted in the flow meters and the oxygen consumption rises to approximately the theoretical for complete combustion to carbon dioxide and water.

(2) Gaseous Oxidation Products.—The gaseous oxidation products of n-octane are carbon monoxide, carbon dioxide and a small amount of some gas absorbed by fuming sulfuric acid, the nature of which was not determined. Its amount was normally less than half that of the carbon dioxide, and may represent only uncondensed organic residues, such as aldehyde vapors. Hydrogen and methane could not be detected in any case examined for these gases.



◉, O_2 reacted; ○, *CO* produced; +, CO_2 produced.

Fig. 2.—Normal octane (theoretical air/fuel ratio).

Although there is an appreciable consumption of oxygen between 200 and 270°, the gaseous oxidation products are very small in amount. Carbon monoxide is practically absent until temperatures just below 270° are reached. Carbon dioxide rises regularly from zero at 200° to about 0.4 mole at 270°.

The change in reaction character noted above, occurring at about 270°, is marked by the sudden appearance of carbon monoxide in relatively large amount in the gases. This gas is found consistently after the first pressure surge and within a range of a few degrees progressive samples may be obtained containing no measurable carbon monoxide and quantities greater than one-half mole. By the time the surges cease the gas contains about one mole of carbon monoxide per mole of octane. Thereafter the carbon monoxide increases almost mole for mole with the oxygen consumption and at 650° it is present to the extent of 3.5 moles.

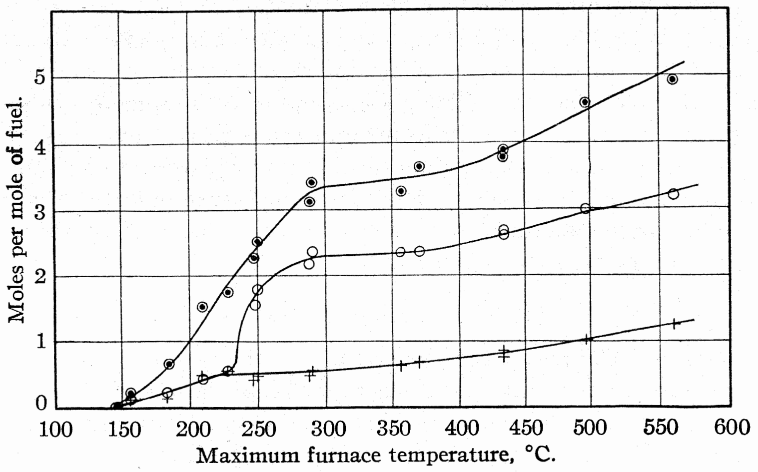
Entrance into the second stage of reaction (at 270°) makes no change in the rate of carbon dioxide production. The amount of this gas rises regularly until it reaches one mole at 400°, after which it remains practically constant. This appears to be the case under all conditions of heating. With the incidence of the third stage (above 650°), the carbon monoxide is reduced to a very low figure and is replaced by carbon dioxide.

(3) Luminescence.—The oxidation of octane is luminescent in certain stages. The first temperature zone, 200–270°, does not show luminescence. The entrance into the second zone may be noticed in the dark by the sudden filling of the tube with a feeble white glow which appears to move counter current to the gas. It forms repeatedly, coincident with the pressure surges, dying away completely in the intervals between them. As the temperature rises, the intervals between flashes grow successively shorter, the initial point of the flash apparently moving toward the inlet point. Ultimately the glow becomes stationary on the gas inlet, where it remains up to 650°. The high temperature pulsations, above 650°, are characterized by a much brighter blue flash which seems to move in the same direction as the gas stream. After the passage of the blue flame, the original pale glow of the second stage is still visible at the inlet. When the temperature becomes sufficiently high, the blue flame likewise settles at that point. The phenomena may be observed in reverse order on cutting off the heating current.

Heptaldehyde and Butyraldehyde

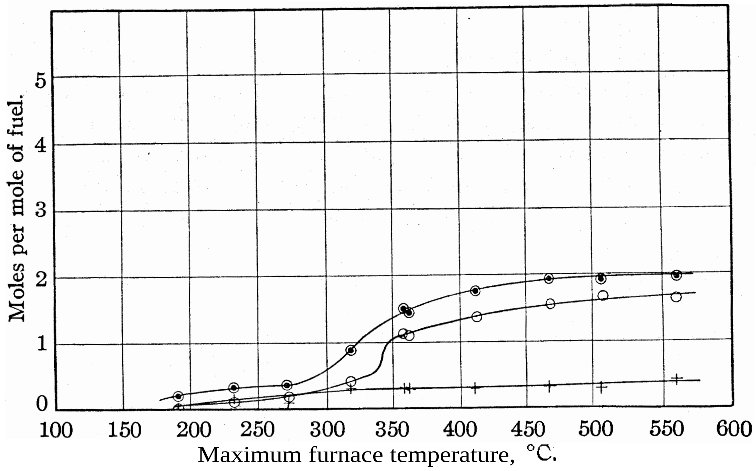
(a) General.—The oxidation of the two aldehydes was studied in a manner similar to that used with n-octane. The same oxygen–nitrogen mixture was used and the fuel rate adjusted to give sufficient oxygen for complete combustion. Thus the oxygen–fuel ratio was about 10–1 for heptaldehyde and about 6–1 for butyraldehyde. The time of passage through the furnace was essentially the same as in the case of n-octane. The curves showing the oxygen consumption and carbon oxides formation for heptaldehyde and butyraldehyde are presented in Figs. 3 and 4, respectively, referring to rising temperature runs.

(b) Heptaldehyde.—Heptaldehyde commences to absorb oxygen at about 150°, the oxygen consumption curve rising steeply, but slightly less so than in the case of octane. At about 300° the curve becomes almost flat; it then rises more gently. In contrast to the behavior of n-octane, both carbon monoxide and dioxide are produced together from the beginning, until at about 235° they are each present to the extent of about 0.5 mole. At this point pulsations in the flow meters occur as with octane, accompanied by luminescence, and carbon monoxide is at once produced in larger quantities, rising to over 2.0 moles at 275°. (That the carbon monoxide formed is produced by oxidation of n-heptaldehyde and not by thermal decomposition was proved by experiments with both heptaldehyde and butyraldehyde made in the absence of oxygen, in which carbon monoxide was not observed at the temperatures in question.) As in the case of octane, also, the carbon dioxide is unaffected by this critical point and it proceeds to rise at the same rate at least up to 570°.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 3.—Normal heptaldehyde (theoretical air/fuel ratio).



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 4.—Normal butyraldehyde (theoretical air/fuel ratio).

The high temperature pulsations, observed with heptaldehyde under somewhat different conditions, were not encountered in these experiments.

(c) **Butyraldehyde.**—The oxidation of butyraldehyde presents the same general features as that of heptaldehyde. It exhibits, however, a long period (200–335°) over which there is a very slight oxygen absorption, with small amounts of carbon monoxide and dioxide. A sharp rise in carbon monoxide occurs at 335°, corresponding to flow meter pulsations. These pulses, however, are very feeble and the temperature range of their duration is very short. The carbon dioxide remains almost constant after this stage, at about 0.3 mole. The high temperature pulsations were not observed in these experiments, in which the maximum temperature was 560°. No luminescence observations were made.

IV. Discussion of Results

(a) General Course of the Reaction.—So many possibilities exist as to the reactions which may take place in the oxidation of as complex a molecule as that of n-octane, and so involved do the phenomena described above appear that it seemed at first most unlikely that the data could be interpreted by any simple set of reactions. Careful consideration of the data, however, led to the conclusion that the reaction proceeds below 650° practically entirely according to a very simple mechanism, and all phenomena observed may be accounted for on this basis. The nature of the reaction above 650° will be discussed below.

The early appearance of aldehyde and water among the reaction products, the invariable presence of considerable aldehyde under all conditions and the general similarity of the oxidation curves of n-octane and the aldehydes suggest strongly that the primary oxidation product of octane is an aldehyde, and that this aldehyde is further oxidized with the formation of other aldehydes of lower molecular weight. The simple hypothesis was therefore made that the oxidation of n-octane proceeds according to the following steps:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + O_2 = CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + H_2O \quad (1)$$

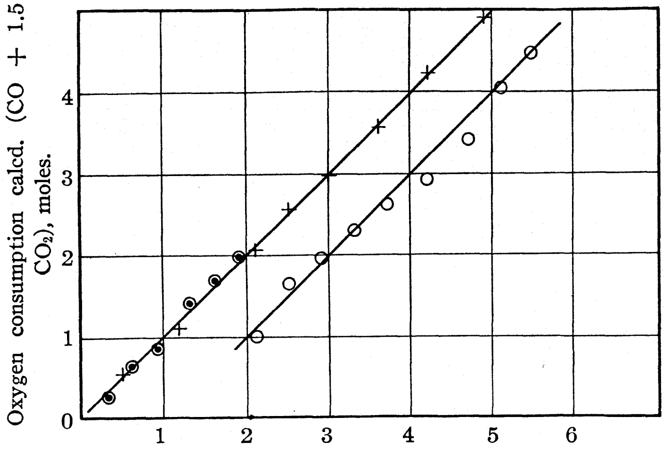
Main reaction, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + O_2 =$
$CH_3CH_2CH_2CH_2CH_2CH_2CHO + H_2O + CO$ (2a)

Side reaction, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + 1.5\,O_2 =$
$CH_3CH_2CH_2CH_2CH_2CH_2CHO + CO_2 + H_2O$ (2b)

Reaction (2) was assumed to continue in the same way, yielding each time an aldehyde of the next lower number of carbon atoms to that oxidized.

This hypothesis was tested as follows. (I) According to the assumptions above, the oxidation of n-octane differs from that of an aldehyde only by the amount of oxygen necessary to convert octane to octaldehyde. Therefore, under conditions in which no unoxidized octane remains, the number of moles of oxygen consumed by n-octane should be greater by one mole than that consumed by heptaldehyde or butyraldehyde for corresponding quantities of carbon monoxide and carbon dioxide formed. The results of calculations based on the curves of Figs. 2, **3** and 4 are given in Fig. 5, in which the sum of the moles of carbon monoxide and 1.5 times the moles of carbon dioxide is plotted against the experimental oxygen consumption. It is clear that the curve for heptaldehyde and butyraldehyde differs from that of n-octane by a figure very close to unity.

(2) The total oxygen consumed by *n*-octane at any temperature should, therefore, be the sum of unity (Reaction 1) plus the moles of carbon monoxide produced (Reaction 2a) plus 1.5 times the moles of carbon dioxide produced (Reaction 2b); while for heptaldehyde and butyraldehyde the total oxygen consumed should be the sum of the moles of carbon dioxide produced plus 1.5 times the moles of carbon dioxide produced. Calculations were made accordingly and the data are compared in Fig. 6 with the experimental data for oxygen consumed. The agreement is surprisingly good, considering the complexity of the octane and aldehyde molecules and the number of reaction products which are possible.

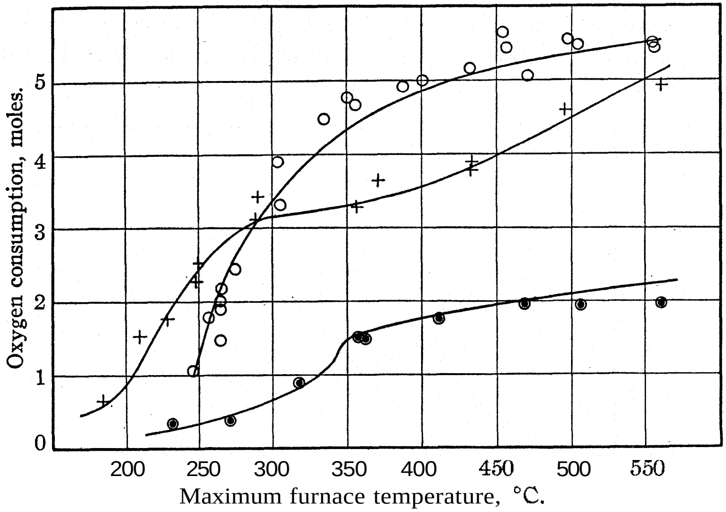


Oxygen consumption, observed, moles.

◉, n-Butyraldehyde; +, *n*-heptaldehyde; ○, *n*-octane.

Fig. 5.

It was found possible to fit the experimental data for *n*-octane reasonably well by making other hypotheses concerning the initial point of attack, but no other hypothesis than the one cited above gave a simple interpretation of the oxidation of the aldehydes as well. Any attack of the aldehyde chain other than at the end would involve more oxygen consumption for a given amount of carbon oxides formation than is found experimentally. Such consumption of oxygen, if appreciable, whether by the formation of water and an unsaturated compound, or the formation of a glycol, or ketone (which would lead to the rupture of the carbon chain at some other position than the end) would make the calculated figures for oxygen consumption diverge from the experimental more widely than is found to be the case. Since practically all of the oxygen consumed is accounted for by the reactions in question, it seems reasonable to suggest that the oxidation of *n*-octane in the vapor phase proceeds substantially according to the simple hypothesis postulated above.



Lines—calculations. Points—experimental. +, *n*-Heptaldehyde; ○, n-octane; ◉, n-butyraldehyde.

Fig. 6.

(b) Mode of Initial Attack.—(1) It has been suggested that the initial attack of oxygen upon a hydrocarbon molecule involves the formation of peroxides. The data cited above offer little evidence for or against such an hypothesis, since such compounds would be expected to be unstable and to exist at any one time in very small amount. Traces of substances reacting with aqueous potassium iodide were found in the liquid oxidation products examined, their actual concentration varying very little. It has been pointed out above that their significance is doubtful. It would appear from this that if those substances represent the peroxides supposedly involved in the initial attack of the hydrocarbon, they are involved in the further oxidation of the aldehydes also, since they appear at temperatures where several moles of oxygen are consumed as well as at low temperatures where the primary oxidation is chiefly concerned. Certainly there is no evidence here of their accumulation at any stage of the reaction.

(2) As in the case of other investigations of vapor-phase oxidations no experimental evidence was obtained of the formation of alcohols. This has been explained, by proponents of the hydroxylation theory, by the supposed ready oxidation of such alcohols to aldehydes. The recent work of Layng and Youker[6] on the oxidation of heptyl alcohol (which confirms the authors' experience with ethyl alcohol) has indicated that alcohols are oxidized in the vapor phase with extreme difficulty in the absence of catalysts. It appears, therefore, much more probable that aldehydes and not alcohols are the primary oxidation products.

(c) Formation **of Carbon** Monoxide and **Carbon** Dioxide.—There appears to be a distinct difference in the nature of the reactions forming carbon monoxide and carbon dioxide. The latter reaction is unaffected by the rate of heating, and shows no abrupt change at any point. It does not become a large factor in the total reaction until temperatures above 650° are reached. Apparently it is a side reaction presenting no unusual characteristics and has been so considered by the authors.

The reaction involving the formation of carbon monoxide appears to be of an entirely different type. The suddenness with which it appears at about 270°, the sharp decrease in its temperature coefficient at slightly higher temperatures and its accompaniment by pressure surges and luminescent flashes, suggest that it belongs to the class of photochemical "chain" reactions, to which several simpler types of oxidation reactions have been shown to belong. This is supported by certain of the authors' experiments on the oxidation of *n*-octane in which the reaction tube was filled with glass tubing to increase surface exposure. The formation of carbon monoxide was substantially suppressed under these conditions, while the carbon dioxide formation was little affected. It seems probable that toward the end of Zone 1 activated molecules of some type are beginning to accumulate. That these molecules are those of aldehyde rather than of octane is indicated by (1) the fact that octane oxidizes at these temperatures very readily to aldehyde, and it is therefore present to a very small extent at the exit end of the reaction tube where the luminescent flashes originate; (2) the fact that entirely similar phenomena occur in the oxidation of heptaldehyde and butyraldehyde. The temperature at which they occur with a comparable aldehyde (heptaldehyde) is lower (235° against 270°), but it must be remembered that the concentrations and energy conditions of all reactants are somewhat different in the two cases.

The sudden reaction initiated by these accumulated activated molecules presumably corresponds to the surges and luminescence, the reaction becoming quiescent while fresh accumulation occurs. As the temperature is raised the intervals between the surges become shorter and the reaction is initiated nearer the inlet, finally occurring smoothly at this point.

With heptaldehyde alone the formation of carbon monoxide proceeds slowly at low temperatures without the appearance of surges or lumines-

---

[6] Layng and **Youker,** *Ind. Eng. Chem.*, **20,** 1048 (1928).

cence, probably because at these temperatures accumulation of active molecules is not occurring at a sufficient rate to initiate the sudden intermittent reactions which occur at somewhat higher temperatures.

(d) High Temperature Reaction.—At high temperatures (660–670° for *n*-octane, and higher than 570° for heptaldehyde and butyraldehyde) the oxidation proceeds practically explosively to carbon dioxide and water. When this reaction begins the temperature in the furnace rises rapidly to a point where it is necessary to discontinue the experiments in order to prevent softening of the glass. No detailed study of this phase of the reaction could therefore be made, and it is not possible to state definitely whether or not the fuels burn directly to carbon dioxide and water, or whether the primary oxidation products are further burned at this stage. The fact that the luminescence associated with the carbon monoxide reaction was still visible between the blue flashes of the second type of explosion would seem to argue for the latter explanation. Further discussion of this point will be given in Part II.

The abrupt changes in reaction character occurring at about 270 aqd 650" for n-octane have some similarity to certain phenomena involved in the spontaneous ignition of octane–oxygen mixtures, a matter which will be discussed in a later paper.

(e) Interpretation of the Oxygen Consumption Data.—In the light of the above interpretation of the experimental facts, it is interesting to examine the oxygen consumption curve (Fig. 2) of n-octane somewhat more closely. The first part of the curve (200–250°) must represent largely formation of water and aldehyde, the latter not oxidizing to any great extent until its concentration becomes appreciable. Its oxidation at these temperatures is largely to carbon dioxide (Reaction 2b) and perhaps partially to acid. As the temperature rises, the oxidation to carbon monoxide predominates, the reaction becoming luminescent and more intense (as evidenced by the sharp rise in temperature immediately after mixing). By the time the temperature has reached 400° the reaction has produced largely aldehydes of the order of butyraldehyde or lower, and these are so much more difficultly oxidized than those of higher molecular weight (compare heptaldehyde and butyraldehyde), particularly in the reduced oxygen concentration, that further reaction occurs very slowly as the temperature is raised until this becomes high enough (above 650°) to carry the oxidation completely to carbon dioxide and water. The oxidation of heptaldehyde slows down similarly when lower aldehydes, sufficiently difficult to oxidize, are formed. It is perhaps significant that the slowing down occurs with heptaldehyde when about three moles of oxygen have reacted, as compared with the similar slowing at five moles of oxygen reacted for n-octane. Presumably the nature of the oxidation products at these respective stages is very similar.

The oxygen consumption curves of heptaldehyde and butyraldehyde are somewhat similar to that of n-octane, but the difference in the nature of the early reaction is shown by the fact that in the case of the aldehydes the oxygen consumption corresponds to the carbon oxides formed, while in the case of octane the early stage involves very little of these oxidation products. Altogether it appears that the interpretation of the oxidation phenomena outlined above is in excellent agreement with the experimental facts and affords a simple explanation of most of the phenomena observed.

V. Summary

1. The vapor phase oxidation of n-octane, n-heptaldehyde and *n*-butyraldehyde has been studied in detail.
2. The results may be simply interpreted on the theory that the initial oxidation product of 7%-octane is octaldehyde, which in turn is further oxidized to aldehydes of successively smaller number of carbon atoms, carbon monoxide and some carbon dioxide being simultaneously formed.
3. The existence of luminescent "chain" reactions is indicated, apparently corresponding to the oxidation of the aldehydes to lower aldehydes, carbon monoxide and water.

YONKERS, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS. II

BY L. C. ANDERSON

RECEIVED FEBRUARY 5, 1929 PUBLISHED JUNE 5, 1929

By the combination of spectroscopic and chemical evidence presented in a previous paper[1] it has been shown that the quinonoid modification of 3-methyl-4-hydroxytriphenylcarbinol is not a mixture of the fuchsone and the benzenoid form of the carbinol. Further studies of the absorption spectra of the above-mentioned carbinols, of 3-methoxy-4-hydroxytriphenylcarbinol and of the 5-chloro- and 5-bromo-derivatives of 3-methyl-4-hydroxytriphenylcarbinol have given further evidence of the quinonoid forms of these hydroxytriarylcarbinols.

The quantitative absorption curves of ether solutions of the methanes, benzenoid modifications, quinonoid modifications and the fuchsones of the aforementioned carbinols have been determined and the points in the visible and ultraviolet portions of the spectrum (7600–2350 Å.) at which a maximum and a minimum of energy is absorbed by these solutions have been located. We have found in the curves for some of the quinonoid forms that the absorption band in the violet region and in the ultraviolet region adjacent to the visible is at a position different from that which it has in the corresponding fuchsone (Table I). This is a positive indication in

---

[1] Anderson and Gomberg, THIS JOURNAL, 50, 203 (1928).

itself that the color of our colored carbinol is not due to the presence of small quantities of the fuchsone and hence that this compound must itself be a quinonoid carbinol.

The quinonoid curve as compared to that of the fuchsone is displaced toward the shorter wave lengths in 5-chloro- and 5-bromo-*o*-cresyldiphenylcarbinols and toward the longer wave lengths in 4-hydroxy-triphenylcarbinol. In *o*-cresyldiphenylcarbinol and guaiacyldiphenylcarbinol the displacement is within our experimental error of determining the position of these peaks.

The similarity of the curves of the members within each class, the methanes, the benzenoid carbinols, the quinonoid carbinols and the fuchsones is very striking. As the molecular weight in each group of compounds is increased some of the peaks for the corresponding derivative in each class are shifted toward the longer wave lengths and some are shifted in the direction of shorter wave lengths. The positions of the bands between frequencies 2800 mm.$^{-1}$ and 2600 mm.$^{-1}$ in the curves for the fuchsones and for the quinonoid carbinols are displaced toward the longer wave length as the molecular weights of each type increase, but the displacement bears no simple relationship to the increase of molecular weight.

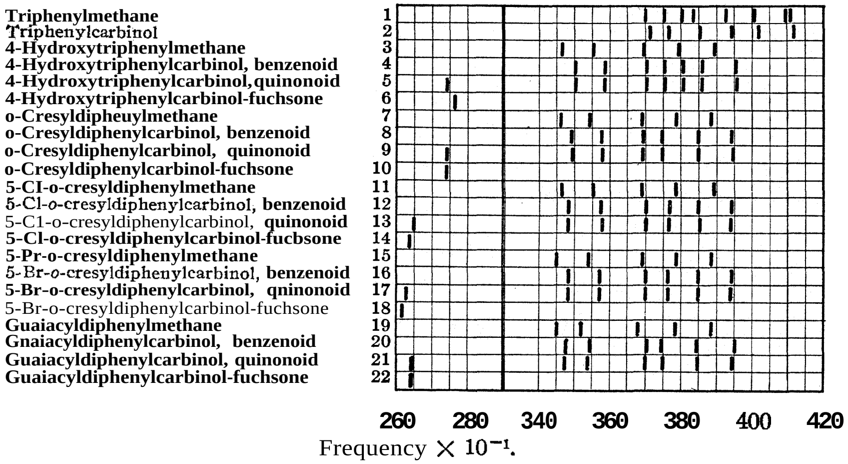


Fig. 1.

Procedure.—The method which we have used in obtaining data for plotting curves to show the quantitative absorption of light by solutions has already been described.[1] For determining the points of maximum and minimum absorption, the relative blackening of the photographed absorption spectra has been measured by means of a Moll recording microphotometer. The spectrograph plate is drawn past the slit of the thermopile at least twice, first, to obtain a curve (a) for the intensity of light in the beam which has passed through the solvent and, second, to obtain a curve (b) for the intensity of light in the beam which has passed through the solution. These curves appear superimposed upon the bromide paper used in the recording instrument. Wherever the two curves have the same slope at a given wave length, there is a point of maximum or minimum absorption. When the solvent curve (a) falls below the solution curve (b) the points of maximum absorption are those wave lengths at which the two curves are farthest apart. Black ink lines ruled upon the plate after exposure and development locate certain frequencies upon the photometer curve and allow any other frequency

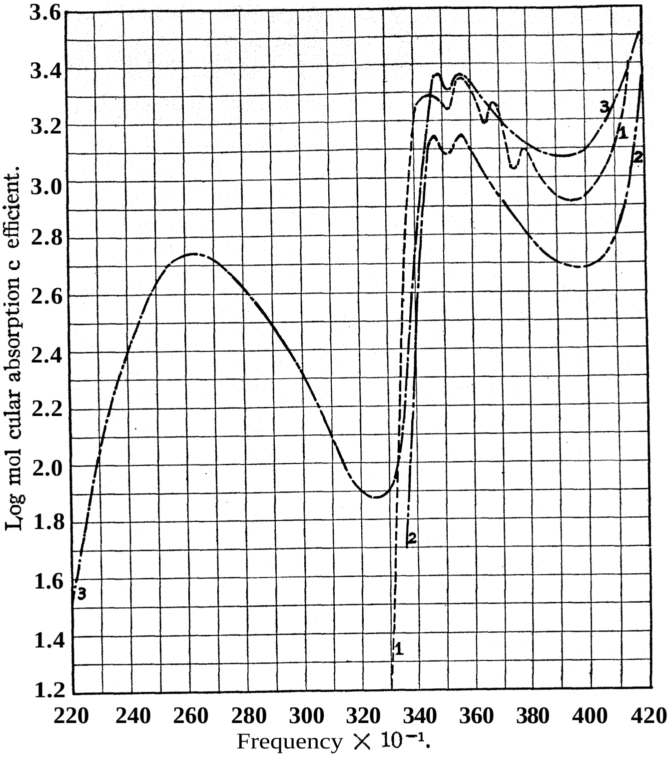


Fig. 2.—5-Chloro-*o*-cresyldiphenylcarbinol: 1, ---, methane; 2, —··—, benzenoid carbinol; 3, —·—, quinonoid carbinol.

Table I

Frequency Numbers

Sample	4-OH-triphenylcarbinol, quinonoid	4-OH-triphenylcarbinol, fuchsone	5-Cl-*o*-cresyldiphenyl-COH, quinonoid	5-Cl-*o*-cresyldiphenyl-COH, fuchsone	5-Br-*o*-cresyldiphenyl-COH, quinonoid	5-Br-*o*-cresyldiphenyl-COH, fuchsone
1	2742	2763	2653	2643	2635	2627
2	2740	2764	2648	2640	2629	2616
3	2738	2767	2650	2640	2628	2621
4	2746	2761	..	..	2630	2617
5	2740					
6	2748	..	..	..	..	
7	2748	..	..	..	..	
Av.	2743	2764	2650	2641	2630	2620

to be found from calibration curves. The instrument was calibrated with the spectrograph and comparator by means of the copper spectrum.

The frequencies at which absorption bands have been located in ether solutions of the compounds under discussion are given in Table II and Fig. 1, which also include additional data upon curves already published. We have previously found by visual observation of the spectrograph plates only the four most prominent absorption bands in triphenylmethane and triphenylcarbinol.[2] By using the microphotometer, we have located other peaks in each of the curves and the positions of the bands as now found agree very well with data which have been published by Orndorff, Gibbs, McNulty and Shapiro upon the solutions of these compounds in alcohol.[3]

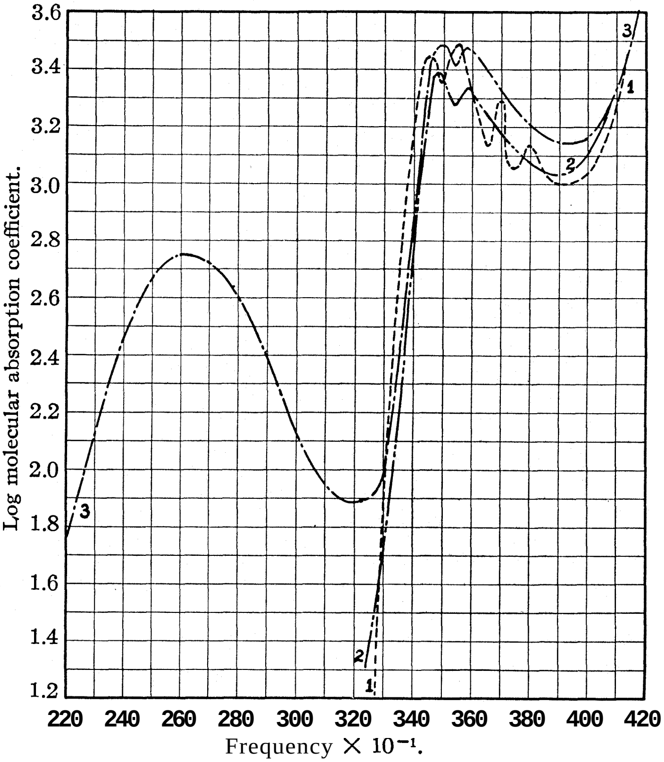


Fig. 3.—5-Bromo-o-cresyldiphenylcarbinol: 1, ---, methane; 2, —··—, benzenoid carbinol: 3, —·—, quinonoid carbinol.

Purification of Materials

3-Methyl-4-hydroxy-5-chlorotriphenylmethane was obtained by reducing the corresponding fuchsone with zinc and acetic acid. The substance was recrystallized

---

[2] Anderson, This Journal, 50, 208 (1928).

[3] Omdorff, Gibbs, McNulty and Shapiro, *ibid.*, 49, 1541 (1927).

from petroleum ether which had been purified until it showed no selective absorption of light between 2300 and 7500 Å.; m. p. 89–89.5°.

3-Methyl-4-hydroxy-5-chlorotriphenylcarbnol, benzenoid tautomer, was prepared by digesting the fuchsone, or the quinonoid form of the carbinol, with *N* potassium hydroxide solution. The solution was filtered and the colorless filtrate was saturated with carbon dioxide. The crystals were washed and dried; m. p. 145–146°.

3-Methyl-4-hydroxy-5-chlorotriphenylcarbinol, quinonoid tautomer, was prepared by dissolving the corresponding fuchsone in glacial acetic acid. Hot water was added to the solution until the acetic acid concentration had been reduced to 60%. The solution was filtered and the filtrate was allowed to cool very slowly. The crystals produced were filtered, washed with fresh solvent and then dried over a saturated solution of potassium hydroxide in an evacuated desiccator; m. p. 133–134°.

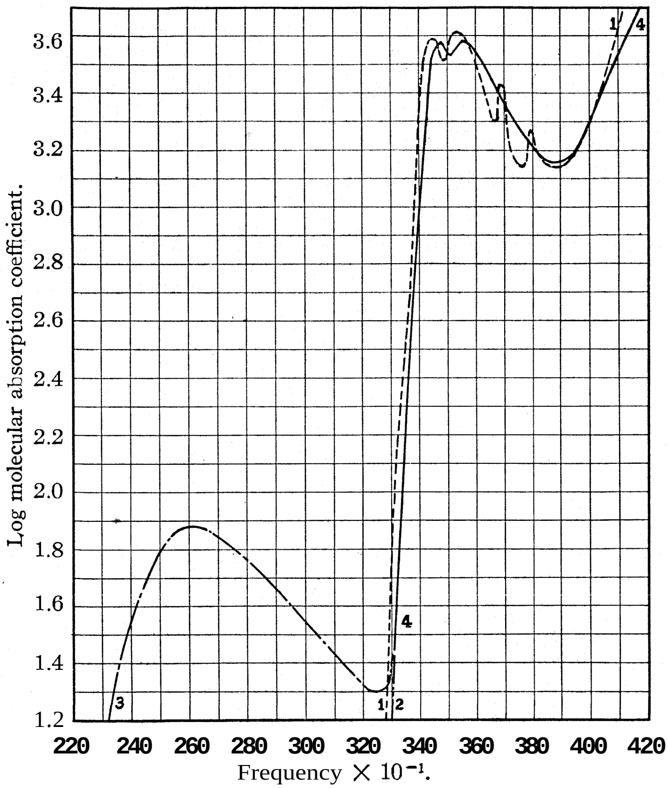


Fig. 4.—Guaiacyldiphenylcarbinol: 1 ---, methane; 2, —··—, benzenoid carbinol; 3, —·—, quinonoid carbinol; 4, —, both benzenoid and quinonoid carbinols.

3-Methyl-4-hydroxy-5-chloroquinodiphenylmethane, that is the fuchsone, was prepared by recrystallizing the corresponding quinonoid carbinol from glacial acetic acid; m. p. 195°.

3-Methyl-4-hydroxy-5-bromotriphenylmethane was prepared by reducing the carbinol with zinc dust and acetic acid. It was crystallized from ether and purified n-hexane; m. p. 119°.

3-Methyl-4-hydroxy-5-bromotriphenylcarbinol, benzenoid tautomer, was precipitated by passing carbon dioxide into a solution of the fuchsone in potassium hydroxide. It was crystallized from ether and optically clear petroleum ether; m. p. 144–145°.

3-Methyl-4-hydroxy-5-bromotriphenylcarbinol, quinonoid tautomer, was prepared by adding to a hot solution of the fuchsone in glacial acetic acid enough hot water to reduce the acetic acid concentration to 60%. The yellow crystals were filtered from the cold solution and were dried over "Ascarite" in a desiccator; m. p. 138–139°.

3-Methyl-4-hydroxy-5-bromoquinodiphenylmethane, the fuchsone of 5-bromo-*o*-cresyldiphenylcarbinol, was recrystallized from hot acetic acid. The crystals were washed with absolute ether until free from acid; m. p. 202–203°.

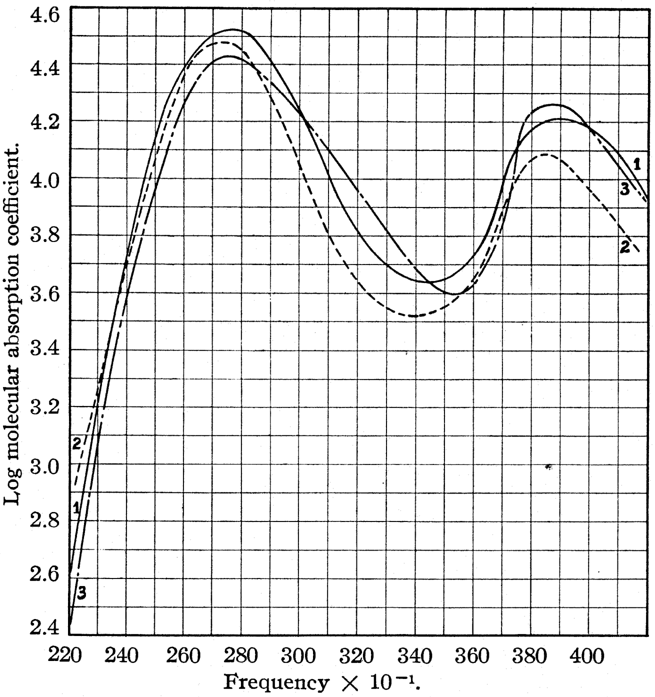


Fig. 5.—Fuchsones of: 1, ———, 5-chloro-*o*-cresyldiphenylcarbinol; 2, ----, 5-bromo-*o*-cresyldiphenylcarbinol; 3, —·—, guaiacyldiphenylcarbinol.

3-Methoxy-4-hydroxytriphenylmethane was prepared by the reduction of the carbinol with zinc and acetic acid. The colorless crystals were recrystallized from ether and n-hexane; m. p. 108°.

3-Methoxy-4-hydroxytriphenylcarbinol, benzenoid tautomer, was purified by several crystallizations from petroleum ether; m. p. 159°.

3-Methoxy-4-hydroxytriphenylcarbinol, quinonoid tautomer, was prepared by recrystallizing the benzenoid tautomer from 60% acetic acid. The bright yellow crystals were filtered off and dried either over saturated potassium hydroxide solution in an evacuated desiccator or over "Ascarite" at atmospheric pressure; m p. 154°. This compound has been previously described as brown crystals which melt at 147°.[4]

---

[4] Gomberg and Van Stone, THIS JOURNAL, 38,1592 (1916).

3-Methoxy-4-hydroxyquinodiphenylmethane, the fuchsone of guaiacyldiphenylcarbinol, was prepaied by crystallizing the quinonoid tautomer from glacial acetic acid. The yellow crystals were heated at 80° for several hours and were then recrystallized from ether; m. p. 182–183°.

TABLE II

FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

	Triphenyl-	4-OH-Triphenyl-	*o*-Cresyldiphenyl-	5-Cl-*o*-cresyldiphenyl-	5-Br-o-cresyldiphenyl-	Guaiacyldiphenyl-
Methane	3700	3463	3462	3465	3452	3451
	3756	3550	3548	3554	3542	3521
	3801	3696	3692	3695	3692	3685
	3831	3793	3787	3789	3789	3787
	3923	3891	3884	3893	3888	3890
	4013					
	4090					
	4108					
Carbinol, benzenoid form	3712	3500	3493	3485	3482	3483
	3764	3582	3577	3575	3581	3548
	3853	3701	3692	3701	3708	3708
	3941	3754	3748	3770	3762	3747
	4015	3802	3849	3850	3851	3858
	4112	3850	3946	3942	3944	3951
		3945				
Carbinol, quinonoid form		2741	2743	2650	2629	2648
		3502	3496	3483	3483	3479
		3589	3583	3580	3575	3548
		3703	3700	3701	3698	3702
		3753	3751	3767	3765	3751
		3806	3854	3853	3850	3848
		3856	3950	3942	3940	3941
		3952				
Carbinol, fuchsone		2764	2740	2641	2620	2648

Summary

1. Curves and tables have been prepared which show the quantitative absorption of ultraviolet light by ether solutions of the methane, the benzenoid carbinol, the quinonoid carbinol and the fuchsone of each of the following compounds: 5-chloro-o-cresyldiphenylcarbinol, 5-bromo-o-cresyldiphenylcarbinol and guaiacyldiphenylcarbinol.

2. Data have been tabulated which supplement those already published upon the quantitative absorption of light by ether solutions of triphenylmethane, triphenylcarbinol and the methane, benzenoid carbinol, quinonoid carbinol and the fuchsone of each, 4-hydroxytriphenylcarbinol and the o-cresyldiphenylcarbinol.

3. Further evidence based on spectroscopic data is presented to prove the existence of a quinonoid modification of hydroxytriarylcarbinols.

ANN ARBOR, MICHIGAN

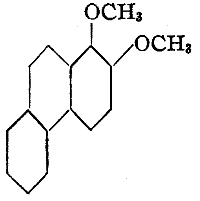
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

1,2-PHENANTHRENEQUINONE

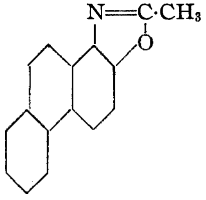
BY LOUIS FREDERICK FIESER

RECEIVED FEBRUARY 8, 1929 PUBLISHED JUNE 5, 1929

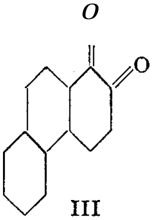
Having found a convenient method of preparing 3,4-phenanthrenequinone from 3-phenanthrol,[1] a similar series of reactions was applied to 2-phenanthrol in the hope of obtaining another isophenanthrenequinone. On reducing with sodium hyposulfite the dyestuff produced by coupling 2-phenanthrol with diazotized sulfanilic acid, an amino-2-phenanthrol was obtained in excellent yield, and the conversion of this substance into a quinone was nearly quantitative. Since both the diacetate and the triacetate of the new amino-2-phenanthrol are easily converted by thermal decomposition into an oxazole derivative, it may be concluded that the coupling has taken place in the ortho position, that is, in either the 1- or the 3-position. Thanks to the valuable synthetical work of Pschorr, a distinction between these two possibilities is not difficult. A dimethoxyphenanthrene was obtained by reducing the phenanthrenequinone and methylating the reduction product. This substance, which must have the structure of either 1,2-dimethoxyphenanthrene or 2,3-dimethoxyphenanthrene, proved to be different from the compound synthesized by Pschorr and Buckow[2] and known to have the structure of the 2,3-isomer. The new substance is thus 1,2-dimethoxyphenanthrene, I, and corresponding structures may be assigned to the oxazole derivative, II, and to the quinone, III.



I



II



III

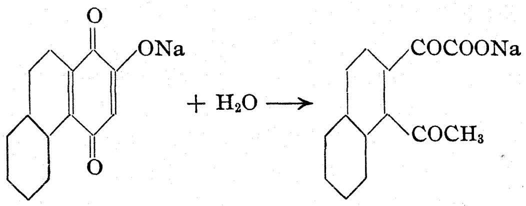
The marked chromophoric character of an isophenanthrenequinone nucleus in comparison with 9,10-phenanthrenequinone was noted in the case of the 3,4-isomer; this is also true of 1,2-phenanthrenequinone, for the substance forms large needles which are brilliant red in color. The similarity between the two isophenanthrenequinones is quite pronounced, and in all but one instance the reactions of 1,2-phenanthrenequinone and of its derivatives follow an entirely normal course. A description of these reactions may be found in the Experimental Part, and it will suffice at this time to call attention to the fact that the hydrolytic cleavage of an hydroxyquinone, noted for the first time in the case of 3-hydroxy-1,4-

---

[1] Fieser, THIS JOURNAL, 51, 940 (1929).

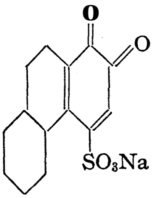
[2] Pschorr and Buckow, Ber., 33, 1831 (1900).

phenanthrenequinone,[1] takes place with great ease with the isomer, 2-hydroxy-1,4-phenanthrenequinone, IV; the reaction being represented as

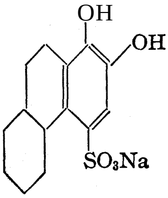


IV V

An interesting deviation from the behavior of other quinones was observed in studying the properties of sodium 1,2-phenanthrenequinone-4-sulfonate, VI. The substance was prepared from the hydroquinone, VII, which, in turn, resulted from the addition of sodium bisulfite to 1,2-phenanthrenequinone. Judging by the properties of other compounds of similar structure, one might expect that VI would react with aromatic



VI



VII

amines in such a way that the sulfonate group would be replaced by an arylamino group. Thus the following compounds all yield water-insoluble anilino- or *p*-toluidinoquinones on reaction with the corresponding amine: 1,2-naphthoquinone-4-sulfonate,[3] 1,2-anthraquinone-4-sulfonate,[4] 3,4-phenanthrenequinone-1-sulfonate,[1] 6,7-indazolequinone-4-sulfonate,[5] and 2-phenyl-benzotriazole-4,5-quinone-7-sulfonate[6] The normal reaction of such quinones with alkali involves, so far as is known,[5] the replacement of the sulfonate group by hydroxyl. 1,2-Phenanthrenequinone-4-sulfonate, on the other hand, undergoes a disproportionation when treated either with p-toluidine or with alkali. On adding alkali to a cold, aqueous solution of the quinone, the color changes at once from red to pale yellow and the solution is now found to contain the hydroquinone, VII. A quantitative study of the reaction, carried out in an indifferent atmosphere and under conditions permitting the detection of any hydrogen peroxide or oxygen which might be formed, showed that one molecule of the hydroquinone results from two molecules of the quinone and that no oxidation

---

[3] Boniger, Ber., 27, 25 (1894).

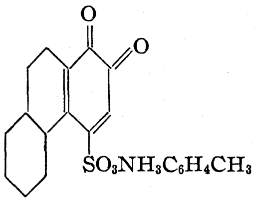
[4] Fieser, THIS JOURNAL, 50,470 (1928).

[5] Fieser, *ibid.*, 48, 1103 (1926).

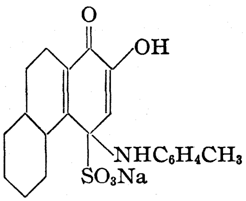
[6] Fieser and Ames, *ibid.*, 49,2614 (1927).

products of water are produced. Thus, while an organic oxidation product was not isolated, there can be little doubt that such a product is formed and that the reaction is of the Cannizzaro type. This reaction is not unusual for all quinones, but only for the particular type of sulfonated quinone under discussion. The unusual feature is that the normal replacement reaction does not occur.

The exceptional character of 1,2-phenanthrenequinone-4-sulfonic acid is even more evident in the reaction with p-toluidine. In neutral aqueous solution a disproportionation again takes place and the p-toluidine salt of the hydroquinone, VII, may be obtained by acidifying the solution. In the presence of mineral acids the disproportionation does not occur, but even under these conditions the replacement of the sulfonic acid group by the p-toluidino group does not take place, for the only reaction product is the *p*-toluidine salt of the quinone-sulfonic acid, VIII.



VIII



IX

The remarkable stability of the sulfonic acid group of this one quinone is probably due to the spatial arrangement of the molecule, for the presence of a benzene nucleus adjacent to the sulfonic acid group is the only structural feature which distinguishes the quinone from all of the similar compounds listed above. If it is supposed that the formation of a p-toluidinoquinone involves, as the first step, the 1,4-addition of the amine to a sulfonated quinone, the influence of the neighboring phenylene group in preventing the formation of an intermediate addition product, IX, is understandable, and this hypothesis appears to afford the most plausible explanation of the phenomenon.

Experimental Part[7]

1-Amino-2-phenanthrol.—The coupling of 2-phenanthrol with diazotized sulfanilic acid and the reduction of the dye by means of sodium hyposulfite proceeded in so nearly the same manner as in the case of 3-phenanthrol[1] that it is only necessary to state the modifications of the method already described, which are required in the present instance. The chief difference is that somewhat more water is required to dissolve sodium 2-phenanthrolate and l-amino-2-phenanthrol hydrochloride than the isomers. The azo compound was first prepared by Werner and Rekner.[8] Like these investigators, I was unable to obtain it in a crystalline condition; the coupling reaction gave a

---

[7] The Dennstedt contact star was employed in carrying out most of the analyses here reported, compare ref. 1, footnote 11.

[8] Werner and Rekner, *Ann.,* 321,307 (1902).

very viscous, colloidal solution of the dye. On reduction with hyposulfite, the aminophenanthrol separated in a very finely-divided condition but the solution filtered without difficulty. The product was often pink, rather than colorless, but this did not interfere with the preparation of the pure hydrochloride. In converting the amine into its salt, it was found expedient to use 6-7 liters of water and 130 cc. of concentrated hydrochloric acid to dissolve the material obtained from 97 g. of 2-phenanthrol. The yield was very close to the theoretical amount.

The free amine was obtained by drying the crude product on a porous plate and crystallizing it from alcohol containing a little sulfur dioxide. It formed glistening plates which were somewhat gray, but which have not undergone further change in nearly a year. The substance begins to darken at about 210°, and there is no definite point of decomposition It dissolves well in alcohol, but is only very sparingly soluble in benzene or ether. The xylene solution darkens on boiling.

Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.35; H, 5.30. Found: C, 80.08; H, 5.51.

1-Amino-2-phenanthrol Hydrochloride.—The salt was purified for analysis by crystallization from an alcoholic solution to which considerable hydrochloric acid was added. A cotton-like mass of colorless micro-needles was thus obtained. The sample became slightly gray during drying; it decomposes in the vicinity of 250". The salt is only moderately soluble in water, but very readily soluble in alcohol. It gives a cherry-red solution on warming with concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_{12}ONCl$: C, 68.42; H, 4.93. Found: C, 68.59; H, 5.28.

The Acetylation of 1-Amino-2-phenanthrol

When the amine is heated with acetic anhydride for about three minutes, a thick paste consisting chiefly of crystals of the N-monoacetate results. If the heating is continued until the crystals just dissolve, the solution contains chiefly the diacetate, together with a little of the triacetate. Prolonged boiling, preferably with the use of sodium acetate as a catalyst, leads to the complete acetylation of the amine. Both the diacetate and the triacetate are converted quantitatively into the N-monoacetate on boiling the alcoholic solutions with hydrochloric acid. Thus this compound may be prepared from a mixture of the diacetate and the triacetate, while the triacetate is most conveniently prepared from the monoacetate.

1-Amino-2-phenanthrol Diacetate.—A mixture of 1 g. of the amine and 10 cc. of acetic anhydride was boiled until the crystals of the monoacetate just dissolved and the solution was cooled and poured into water. The product was crystallized from benzene until the melting point became constant at 222° (227°, corr.). The compound formed a cotton-like mass of fine, colorless needles; yield, 0.5 g. It is only sparingly soluble in benzene and insoluble in acids or alkalies.

Anal. Calcd. for $C_{18}H_{15}O_3N$: C, 73.69; H, 5.16. Found: C, 73.38; H, 5.18.

1-Acetylamino-2-phenanthrol.—The method of acetylation just described yields, as the crude product, a mixture of the di- and triacetates suitable for the preparation of the monoacetate, but it is convenient to add a little sodium acetate in order to hasten the reaction. The crude product, without being dried, was dissolved in alcohol, hydrochloric acid was added and the solution was boiled until there was no increase in the quantity of the glistening white plates of the monoacetate. The yield was practically quantitative. The substance may be dissolved in alkali and recovered without change. It is very sparingly soluble in alcohol, benzene or glacial acetic acid and it crystallizes from nitiobenzene, in which it dissolves readily, in the form of plates melting at 295°.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.46; H, 5.22. Found: C, 76.56; H, 5.12.

I-Amino-2-phenanthrol **Triacetate.**—A mixture of equal parts of the monoacetate and fused sodium acetate with ten parts of acetic anhydride was boiled for one and one-half hours and the solution was then poured into water. The triacetate soon separated in the form of a clean solid melting at 122–123°, and the yield was close to that called for by theory. The substance, which dissolves very readily in alcohol or benzene, is best crystallized from ligroin, when it forms colorless scales melting at 125".

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.62; H, 5.11. Found: C, 71.63; H, 5.01.

Oxazole Derivative of 1-Amino-2-phenanthrol (II).—This compound was obtained from both the diacetate and the triacetate. The material was heated in a distilling flask with a sealed-on receiver until no more acetic acid or anhydride was given off and then distilled at a pressure of 3 mm. The oxazole is very readily soluble in alcohol, benzene or ligroin, but insoluble in acids or alkalies. It was crystallized from methyl alcohol, forming slender colorless needles on rapidly cooling the solution, and very large thick needles on slow cooling. The substance melted at 120°.

Anal. Calcd. for $C_{16}H_{11}ON$: C, 82.37; H, 4.76. Found: C, 82.03; H, 4.95.

Oxidation Experiments.—Attempts to convert the above oxazole derivative into a quinone were unsuccessful. It appeared that the substance is oxidized with difficulty and that, when the reaction does proceed, it quickly passes beyond the quinone stage. The triacetate of 1-amino-2-phenanthrol, treated with an equal weight of chromic acid in glacial acetic acid solution at 60°, gave a very small amount of a substance which appeared to be a quinone (orange color, green solution in alcoholic alkali), but the only product isolated in any quantity was aminophenanthrol diacetate. Thus the partial hydrolysis of the starting material is at least partly responsible for the failure to obtain a good yield of the quinone in this case.

1,2-Phenanthrenequinone

In preparing this quinone it is advisable to start with 2-phenanthrol and to carry out the various operations, including the oxidation of the aminophenanthrol, without isolating any of the intermediates. Quantities of the materials found convenient for the preparation are given below, while reference has already been made to the details of the coupling reaction and the reduction.

To a solution of 30 g. of 2-phenanthrol and 18.5 g. of sodium hydroxide in about 1 liter of water, ice was added until the mixture half filled a 4-liter beaker. After coupling with a suspension of an equivalent quantity of diazotized sulfanilic acid, in about 1 liter of water, reduction with a solution of sodium hyposulfite was carried out, the aminophenanthrol was collected and then washed back into the beaker. A little sodium bisulfite was added, the volume was made up to 2.5 liters with boiling water and 40 cc. of concentrated hydrochloric acid was added. The material rapidly passed into solution and left only a trace of residue on filtration. The solution was cooled rapidly, with stirring, in order that the amine hydrochloride which separated should come down in a finely-divided condition. After cooling to room temperature, an aqueous solution of 13.3 g. (1.3 Th.) of chromic acid and 11 cc. of concentrated sulfuric acid was added all at once. A dark precipitate was first produced, but this soon changed to a bright, finely-divided red product. In order to facilitate the collection and washing of this material, the mixture was heated to the boiling point, while stirring constantly, for this treatment serves to increase greatly the particle size without destruction of the quinone. Thoroughly. washed and dried, the 1,2-phenanthrenequinone formed a red powder weighing 29–31 g. (90–96%). This material is not quite pure, but it is satisfactory for many reactions.

The quinone was purified by crystallization from toluene, in which it dissolves fairly readily. A small amount of black material remained undissolved, and the solution was at first dull red; but by further crystallization from this solvent, with the use of animal charcoal, a brilliant red product was obtained which crystallizes in the form of needles. The substance is moderately soluble in alcohol or benzene and readily soluble in glacial acetic acid; it crystallizes well from the red solutions in all of these solvents. It softens at about 195° and melts with decomposition at 216° (222° corr.). The reaction with concentrated sulfuric acid is both characteristic and beautiful: the solution is at first brilliant blue in color but changes within a few seconds to an intense sap-green. In this respect the substance is similar to 3,4-phenanthrenequinone, though the two are easily distinguished by the test. The two quinones, in crystalline condition, are almost identical in appearance, but the 1,2-isomer is much the less soluble of the two.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Found: C, 80.62; H, 4.08.

1,2-Dihydroxyphenanthrene.—On warming an aqueous suspension of the quinone, best in the finely-divided condition in which it is first obtained, with a solution of sodium hyposulfite, the material soon became reduced and a somewhat dark precipitate of the hydroquinone was formed. Enough alcohol was added to bring the material into solution at the boiling point and the solution, after treatment with animal charcoal, was filtered and quickly cooled. The hydroquinone was thus obtained in the form of small, colorless needles which, however, darkened considerably on long storage. The compound melts at 178°. The alkaline solution is at first yellow, but the action of the air soon gives a precipitate of a green quinhydrone, or its salt. In a solution of alcoholic alkali the oxidation soon proceeds beyond this stage and the red sodium salt of 2-hydroxy-1,4-phenanthrenequinone soon separates.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.80. Found: C, 79.63; H, 4.77.

1,2-Dimethoxyphenanthrene.—1,2-Dihydroxyphenanthrene was methylated in an atmosphere of nitrogen with dimethyl sulfate and alkali. The product was distilled at diminished pressure and crystallized from ligroin. It forms feathery clusters of short. colorless needles melting at 102°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.60; H, 5.88.

Attempts to convert the compound into a quinone were not successful,

2-Hydroxy-1,4-phenanthrenequinone

1,2,4-Triacetoxyphenanthrene.—This compound was easily obtained by applying the Thiele reaction to 1,2-phenanthrenequinone, but the yield was poor. Twenty-five grams of the finely powdered quinone was slowly stirred into a mixture of 160 cc. of acetic anhydride and 5 cc. of concentrated sulfuric acid, while cooling to room temperature. The quinone dissolved rapidly to give a dark brown solution, from which crystals of the triacetoxyphenanthrene began to separate within a few minutes. After standing for two hours, the mixture was cooled well, the walls of the vessel were scratched to relieve supersaturation and the product was then collected and washed with glacial acetic acid and with alcohol. The material (16 g.) melted at 180–182°, and gave 15.5 g. (36%) of pure 1,2,4-triacetoxyphenanthrene on crystallization. The acetic anhydride mother liquor, on decomposition with water, gave a very dark-colored, tarry product which is not profitably worked for the triacetate. It may be heated with alcohol and sodium hydroxide solution, when the sodium salt of 2-hydroxy-1,4-phenanthrenequinone separates, due to hydrolysis and oxidation. This salt, though mixed with much black material, is easily converted into the pure hydroxy compound, for the impurities are insoluble in water. In this way it is possible to obtain the equivalent of about 5 g. of the triacetate. 1,2,4-Triacetoxyphenanthrene crystallizes well from glacial acetic acid, benzene or benzene–ligroin and forms colorless needles melting at 186° (189°, corr.).

Anal. Calcd. for $C_{20}H_{16}O$: C, 68.16; H, 4.58. Found: C, 68.23; H, 4.65.

2-Hydroxy-1,4-phenanthrenequinone.—Since this quinone is destroyed very rapidly by boiling its alkaline solution, special precautions must be observed in preparing it by the hydrolysis and oxidation of the above triacetate. In the method which follows the process of hydrolysis, which requires either an elevated temperature or a prolonged period of reaction, was carried out separately, and then advantage was taken of the ease of oxidation of the cold hydroquinone solution and the slight solubility of the sodium salt of the oxidation product.

A suspension of 12 g. of 1,2,4-triacetoxyphenanthrene in 100 cc. of alcohol was swept free of oxygen with a stream of nitrogen and 50 cc. of oxygen-free 6 N sodium hydroxide was added. On warming to the boiling point, hydrolysis soon took place with the formation of an orange solution. The solution was then cooled, diluted with 100 cc. of water and treated with a stream of air until there was no further increase in the amount of the red precipitate of the sodium salt of 2-hydroxy-1,4-phenanthrenequinone. This material was then collected, washed with alcohol and dried; yield, 7.4 g. (88%). In order to obtain the free hydroxy compound, the sodium salt was added to *2* liters of boiling water, the solution was stirred vigorously in order to bring the salt into solution as quickly as possible and then filtered into dilute sulfuric acid. The quinone was thus obtained in a pure condition, in the form of an orange-yellow mass of micro-needles.

2-Hydroxy-1,4-phenanthrenequinone is only sparingly soluble in water, very readily soluble in alcohol and readily soluble in benzene or glacial acetic acid. The yellow solutions deposit cotton-like clusters of small, orange-yellow needles melting at 188° (190°, corr.) with decomposition. The solution in concentrated sulfuric acid is intensely green, the alkaline solution is red.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.78; H, 3.62.

2-Methoxy-1,4-phenanthrenequinone.—The hydroxy compound is easily converted into the ether by boiling with methyl alcohol and hydrogen chloride. The ether separates from the hot solution in the form of long, yellow needles and the yield is quantitative. The ether is easily hydrolyzed by hot alkali; it is moderately soluble in alcohol and readily soluble in benzene; m. p., 172.5".

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.37; H, 4.27.

The Allylation of 2-Hydroxy-1,4-phenanthrenequinone

This reaction proceeded less smoothly than is usually the case, and a considerable amount of tarry material was not identified. A suspension of 4.9 g. of the silver salt of the quinone in 70 cc. of benzene was boiled with 2 g. of allyl bromide for one hour and the benzene solution of the reaction products was concentrated in vacuum to a very small volume. From the very dark red solution there separated a solid product which was rather tarry but which was obtained in a fairly clean condition by washing with benzene. This was triturated with successive portions of dilute ammonia solution until no further material dissolved. The residue was found to contain chiefly 4-alloxy-1,2-phenanthrenequinone, of which 1 g. (26%) was obtained, while 1 g. of the product of C-alkylation was recovered from the ammonia solution.

4-Alloxy-1,2-phenanthrenequinone.—The crude material, which is readily soluble in alcohol or benzene, was crystallized repeatedly from ligroin. It formed dark red rather ill-formed needles melting at 128°. The quinone dissolves easily in sodium bisulfite solution with the formation of a rather sparingly soluble addition product.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77 25; H, 4.58. Found: C, 76.93; H, 4.64.

3-Allyl-2-hydroxy-1,4-phenanthrenequinone.—On crystallization from ligroin, in which it dissolves readily, the compound forms long, slender orange needles melting at 157°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.27; H, 4.85.

The alkaline solution of this quinone is grape-purple but the color disappears completely on boiling the solution for a short time and the acidification of the colorless solution causes the separation of an oil. The quinone thus appears to behave in a mannet similar to that described befow for 2-hydroxy-1,4-phenanthrenequinone. The allyl derivative dissolves in concentrated sulfuric acid with the formation of an intensely green solution; a dark purple-red substance precipitates on adding water.

The Cleavage of 2-Hydroxy-1,4-phenanthrenequinone by Alkali

In describing the preparation of this quinone, it was stated that the substance is extremely sensitive to the hydrolytic action of hot alkali. An aqueous solution of the pure sodium salt rapidly loses its color on boiling and becomes pale yellow, and the change is hastened by the presence of an excess of alkali. On acidifying the hot solution, after it has been somewhat concentrated, the cleavage product crystallizes in the form of large, well-formed, somewhat yellow plates. The substance has the composition of the starting material plus the elements of one molecule of water, and the properties of an α-keto acid. It is in every way similar to the isomeric substance obtained in the same way from 3-hydroxy-1,4-phenanthrenequinone,[1] and the structure follows from the same considerations as those detailed in the earlier paper. The cleavage occurs more rapidly in the present case than with the 3-hydroxyquinone.

I-Aceto-2-naphthyl-glyoxylic Acid (V).—The cleavage product is readily soluble in water and crystallizes best from an acidified aqueous solution. Several crystallizations are required to remove a trace of yellow coloring matter, though the melting point is little affected by the process. The compound melts at 181° with the evolution of carbon dioxide.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.41; H, 4.16. Found: C, 69.02, 69.48; H, 4.24, 4.28. *Neut. equiv.* Subs. 0.2038: 6.81 cc. of 0.1242 N $Ba(OH)_2$. Calcd. for $C_{14}H_{10}O_4$: mol. wt., 242.1. Found: 240.7.

The methyl ether was prepared by esterification with methyl alcohol and hydrogen chloride. It dissolves very readily in alcohol or benzene and fairly readily in ligroin. It is easily purified by the use of the latter solvent, but the crystals are not good; a paste of micro-crystals melting at 112° results.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.19; H, 4.76.

Oxidation of 1-aceto-2-naphthyl-glyoxylic acid with hydrogen peroxide in alkaline solution gave naphthalene-1,2-dicarboxylic acid, while the same reagent, in glacial acetic acid solution, yielded 1,2-naphthindanedione. The oxidation products are thus the same as those obtained from the isomeric acid, 2-aceto-1-naphthyl-glyoxylic acid.' The present reactions were carried out in the same manner and the products were carefully compared and their identity established.

1,2-Phenanthrenequinone-4-sulfonic Acid

Salts of 1,2-Dihydroxyphenanthrene-4-sulfonic Acid.—The addition of sodium bisulfite to 1,2-phenanthrenequinone does not proceed as smoothly as is usually the case with *o*-quinones of this type because some of the material always undergoes reduction to the hydroquinone before the addition reaction has gone to completion. When the quinone was treated with concentrated bisulfite solution, very little reaction of any sort took place until a small volume of alcohol was added. Nearly all of the material then dissolved, but a considerable part of it was converted into 1,2-dihydroxyphenanthrene, which soon separated in an impure condition. The formation of this substance was to some extent hindered by using a mixture of sodium bisulfite and sodium sulfite.

Twenty grams of 1,2-phenanthrenequinone was ground to a fine paste with 60 cc. of water and a solution of 40 g. of sodium bisulfite and 4 g. of sodium hydroxide in 90 cc. of water was added. The quinone rapidly disappeared, giving a dark brown solution containing some suspended matter. After a few hours it was diluted to a volume of 400 cc., warmed to about 80° in order to coagulate the particles of 1,2-dihydroxyphenanthrene and filtered. A solution of 27 cc. of concentrated sulfuric acid in water was then added, together with a few drops of caprylic acid to prevent foaming, and the sulfur dioxide was boiled off. The solution, on cooling, now deposited crystals of sodium 1,2-dihydroxyphenanthrene-4-sulfonate. This material was dissolved in water containing some sodium hyposulfite, and salted out with a solution of sodium chloride. An almost colorless product resulted; yield, 19.7 g. (65%). A further crystallization gave a sample containing the calculated percentage of sodium, though the compound does not crystallize well but forms a faintly gray crystalline powder. It is very readily soluble in water.

Anal. Calcd. for $C_{14}H_9O_5SNa$: Na, 7.36. Found: 7.19.

The potassium salt is somewhat less soluble but it also forms poor crystals. The sample was dried at 80°.

Anal. Calcd. for $C_{14}H_9O_5SK \cdot 2H_2O$: K, 10.73. Found: 10.83.

The p-toluidine salt was precipitated by adding p-toluidine and an excess of hydrochloric acid to a solution of the sodium or the potassium salt. It crystallizes well from water acidified with hydrochloric acid, forming faintly yellow, lustrous plates melting at 240° (248°, corr.), with decomposition. It darkens somewhat on exposure to the sunlight.

Anal. Calcd. for $C_{21}H_{19}O_5NS$: C, 63.45; H, 4.82; S, 8.07. Found: C, 63.25; H, 5.01; S, 8.04.

Sodium **1,2-Phenanthrenequinone-4-sulfonate.**—The oxidation of sodium 1,2-dihydroxyphenanthrene-4-sulfonate in aqueous solution with a slight excess of chromic acid–sulfuric acid solution takes place readily at room temperature, but some caution is necessary in purifying the product for it decomposes rather easily when in an impure condition. The deep red solution which resulted from the oxidation was treated with an equal volume of saturated sodium chloride solution, causing the separation of the red sodium salt of the quinone. This material, which was rather finely divided, was collected and dissolved, while still moist, in boiling water. The solution was filtered without delay, treated with about one-third of its volume of alcohol and at once cooled. This time the quinone separated in the form of fine crystals, so that the material could be thoroughly washed. It was then dissolved in a minimum quantity of water, a small amount of alcohol was added to the filtered solution and crystallization was allowed to proceed slowly. The quinone then separated in the form of large, bright red plates. The pure material shows little tendency to undergo decomposition in solution, but solutions of less pure samples rapidly lose their bright red color on standing, even at room temperature, and deposit a very dark, or even black, product. The quinone dissolves readily in hot water, but it is much less soluble than sodium 3,4-phenanthrenequinone-1-sulfonate. The sample for analysis was dried at 100° in a vacuum.

Anal. Calcd. for $C_{14}H_7O_5SNa \cdot H_2O$: Na, 7.01. Found: 6.76.

The behavior of this quinone toward alkalies and amines is unique. When dilute sodium hydroxide solution is added to a suspension of the quinone in water, the red crystals lose their color at once and become green. On warming the material all dissolves to give a yellow solution. If a saturated solution of the quinone in water is treated with an equal volume of 6 *N* sodium hydroxide, the color changes at once from red to yellow. If such a solution is acidified at once, the red color reappears, but if the alkaline solution is allowed to stand for about one hour, acidification causes only a change to a paler yellow. If this solution is sufficiently concentrated, the sodium salt of 1,2-dihydroxyphenanthrene-4-sulfonate will separate. The identity of the substance was established by adding p-toluidine hydrochloride to the pale yellow solution, when the p-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonate crystallized in the form of plates of characteristic appearance; it was identified by mixed melting point determinations.

The reaction of the quinone with p-toluidine follows a similar course. When a solution of the quinone in hot water was treated with an equivalent quantity of the amine, a very small amount of dark red tar was formed, but in about five minutes the solution lost its red color and became pale yellow. On concentrating the solution and adding hydrochloric acid, the p-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonic acid, which was again identified by melting-point determinations, separated

In order to determine what substance becomes oxidized in the course of the reduction of the quinone in these two cases, the following experiment was carried out. A weighed sample of the quinone was dissolved in water in an oxidation–reduction vessel in which the potential of the solution could be measured. Pure nitrogen was passed through a definite volume of alkali, then into the quinone solution and then into a second oxidation–reduction vessel containing an alkaline solution of sodium anthraquinone-β-sulfonate and its reduction product. Since this solution is very sensitive to oxygen, the presence of even a trace of this gas could be detected by a change in the potential of the solution. After all of the oxygen had been removed from the system, the alkali was transferred under a pressure of nitrogen into the vessel containing the quinone solution. It had seemed possible that either oxygen or hydrogen peroxide might be produced in the reduction of the quinone, but no oxygen was detected even when the mixture of the quinone and alkali was boiled. After the solution had stood for ten to fifteen hours, always protected by an atmosphere of nitrogen, a volume of sulfuric acid calculated to give a $N/10$ acid solution was added and the amount of the hydroquinone present was determined by electrometric titration with a dichromate solution. From 0.2009 g. of the quinone there was found present an amount of hydroquinone equivalent to 0.0980 g. of quinone, which indicates that 48.7% of the quinone had been converted into the hydroquinone. This indicates that one molecule of the hydroquinone is produced from two molecules of the quinone. The conclusion was supported by the results of a somewhat cruder experiment in which the amount of the hydroquinone formed was determined by precipitating it in the form of its p-toluidine salt. From 0.511 g. of the sodium salt of the quinone, there was obtained 0.317 g. of the nearly pure p-toluidine salt (m. p. 234°); on the basis of the above hypothesis, 0.309 g. should result.

The **p-Toluidine** Salt of **1,2-Phenanthrenequinone-4-sulfonic** Acid **(VIII).—The** disproportionation of the sulfonated quinone in a solution containing a basic substance such as sodium hydroxide or p-toluidine does not occur in a neutral or acidic solution. One thus might expect that the quinone would react with p-toluidine in an acidic solution in a manner similar to other sulfonated quinones of the same type, that is, with the formation of a water-insoluble p-toluidine-quinone. It was found, however, that no such substance is produced, but that a simple amine salt of the quinone sulfonic acid is the sole reaction product. The salt was prepared by adding a solution of p-toluidine in an excess of dilute hydrochloric acid to an aqueous solution of sodium 1,2-phenanthrenequinone at the boiling point. On cooling, the salt separated in the form of slender, flat, bright red needles which, washed with a little cold water, were analytically pure. The substance decomposes very easily and it darkened considerably when crystallized even from an acidic solution containing p-toluidine hydrochloride to decrease the solubility. The salt is very readily soluble in water and it decomposes on heating at an indefinite temperature.

Anal. Calcd. for $C_{21}H_{17}O_5SN$: C, *63.77;* H, 4.34. Found: C, *63.58;* H, **4.33.**

Summary

1,2-Phenanthrenequinone has been prepared for the first time and it has been used in securing various other phenanthrene derivatives, notably 2-hydroxy-1,4-phenanthrenequinone and sodium 1,2-phenanthrenequinone-4-sulfonate. The former compound exhibits an interesting type of hydrolytic cleavage by alkalies, observed heretofore in only one other case, while the sulfonated quinone is characterized by a remarkable stability of the sulfonic acid group, a property which appears to be connected with the spatial arrangement of the molecule.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF EPHEDRINE AND STRUCTURALLY SIMILAR COMPOUNDS. II. THE SYNTHESIS OF SOME EPHEDRINE HOMOLOGS AND THE RESOLUTION OF EPHEDRINE

BY RICHARD H. F. MANSKE[1] AND TREAT B. JOHNSON

RECEIVED FEBRUARY 11, 1929 PUBLISHED JUNE 5, 1929

In Paper I of this series the authors described some new reactions which led to the synthesis of ephedrine. For the benefit of anyone desirous of repeating the synthesis emphasis is to be laid on the importance of using highly purified methylamine. Owing to the presence of undetermined impurities in the different preparations supplied for our research the most satisfactory results have been obtained only from Kahlbaurn's hydrochloride of this base.

It was desirable to determine the generality of the reaction and to ascertain its limitations. Thus far the chief drawback has been the difficulty of preparing certain desired 1,2-diketones, although 1-phenylpropane-1,2-dione itself may be easily prepared. The troublesome cases are those in which methoxyl or hydroxyl groups are attached to the benzene nucleus. It has been found that ketonic aldehydes as well as the diketones may be used, and all primary aliphatic amines so far tried have given the expected product. In the case of aniline the product had somewhat indefinite properties, and no ephedrine-like substance was obtained from p-amidophenol.

Details of the synthetic products are given in the annexed table.

It is of some interest to mention that only in one or two cases was there any evidence of the presence of a second isomer, presumably related to ψ-ephedrine. An extensive search was made in the case of the N-ethyl analog of ephedrine but no isomer could be isolated.

The preparation of the p-ethyl derivative (see table) yielded a small

---

[1] Eli Lilly and Company Research Fellow, 1927–1928–1929.

Table I

Substituted Ephedrines

$C_6H_5CH(OH)CH(R)NHC_2H_5$, R =	M. p., °C.[2] HCl salt	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
CH_3	198[3]	6.50	6.32	16.45	16.61
C_2H_5	226	6.10	6.24	15.45	15.53
$C_6H_5CHOHCH(CH_3)NHR$, R =					
CH_2CH_2OH	166	6.05	5.94	15.32	15.50
$C_6H_5CH_2$	184–185	5.05	5.09	12.78	12.83
$C_6H_5CH_2CH_2$	207–208	4.80	4.90	12.16	12.09
$ArCHOHCH(CH_3)NHC_2H_5$, Ar =					
p-Ethylphenyl	208	5.75	5.77	14.56	14.45
2,5-Dimethylphenyl	221	5.75	560	14.56	14.67
p-$CH_3C_6H_4CH(OH)CH_2NHC_2H_5$	208	6.50	6.60	16.45	16.43

quantity of an isomeric base, but since the original starting material for the synthesis, *p*-ethylpropiophenone, was prepared by the Friedel–Crafts reaction, there is the possibility of some o-isomer being present.

Inactive ephedrine forms readily crystalline salts with many optically active acids, among which may be mentioned tartaric, d-camphorsulfonic and mandelic acids. No resolution could be effected with the first two and an attempt to use d-camphoric acid yielded a small amount of crystals which, however, contained only dl-ephedrine. The mandelic acids are very well suited to the purpose, the d-acid-d-base and, conversely, the 1-acid-1-base, compounds being far less soluble in 95% alcohol than the other possible combinations. Three recrystallizations suffice to obtain optically pure products and the yields are good. Incidentally, the resolution of mandelic acid is very readily accomplished by means of natural 1-ephedrine. Furthermore, the authors suggest the use of natural \$-ephedrine to prepare I-tartaric acid from the racemic acid, since Spath and Gohring[4] have shown that dl-\$-ephedrine can be resolved readily by means of the active tartaric acids.

Experimental Part

The compounds described in the table were prepared and isolated as in the case of ephedrine. For the purpose of purification the hydrochlorides were dissolved in a small volume of alcohol; the solution was filtered, evaporated somewhat and treated with a small volume of acetone. Where necessary this procedure was repeated. To obtain the N-β-phenylethyl analog free of β-phenylethylamine, the crude mixture was conveniently recrystallized from a small volume of water, in which the ephedrine salt is sparingly soluble.

The primary amines required in the syntheses were, for the greater part,

---

[2] Melting points are corrected.

[3] Hyde, Browning and Adams, This Journal, 50, 2292 (1928), give the melting point of their product as 190–192°.

[4] Spath and Gohring, *Monatsh.*, 41,319 (1920).

commercial preparations. Benzylamine and β-phenylethylamine were prepared by hydrolyzing the corresponding phthalimides with hydrazine hydrate.[5]

Resolution of dl-Ephedrine.—A mixture of 13.8 g. of dl-ephedrine and 7.7 g. of *d*-mandelic acid was dissolved in 30 cc. of hot 95% alcohol. On cooling the d-ephedrine-d-mandelate crystallized out. After two recrystallizations from a small volume of alcohol the product consisted of colorless, rhombic plates, melting at 170^{e} with previous sintering at 167°. The combined mother liquor yielded a further small amount of this product. The salt as thus obtained was basified with potassium hydroxide and the base was extracted with ether. The ethereal solution was evaporated to a small volume and treated with alcoholic hydrogen chloride. The d-ephedrine hydrochloride as thus obtained melted at 218 to 218.5"and had $[\alpha]_D^{24}$ + 35.6" in 2% aqueous solution; yield, 5.3 g.

The mother liquor from the mandelate of the d-base was basified and the extracted base treated with 7.7 g. of *l*-mandelic acid. The crystalline mandelate was twice recrystallized from a small volume of alcohol; m. p. 170° with previous sintering at 167". The 1-ephedrine hydrochloride obtained from the mandelate melted at 218 to 218.5°, alone or admixed with a purified specimen from Ma Huang, and had $[\alpha]_D^{24}$ —35.5° in 2% aqueous solution; yield, 6.7 g.

It was now possible to obtain a further amount of d- and then I-base from the mother liquor from the mandelate crystallizations by alternate treatment with d- and I-mandelic acid, respectively.

Resolution of Mandelic Acid.—Considerable quantities of mandelic acid were required in the resolution of ephedrine and as far as the authors are aware the most convenient source of d-mandelic acid is from the sparingly soluble cinchonine salt. This process was described almost simultaneously by McKenzie[6] and by Rimbach.[7] McKenzie prepared a number of salts of d- and 1-mandelic acid with various alkaloids and recorded their melting points among other physical properties. Rimbach did not record melting points. Recently Ward, Chrisman and Nicholas: while in agreement with McKenzie in so far as the resolution is concerned, pointed out a discrepancy in the melting points as recorded by the latter for the quinine salts of the d- and 1-acids. The present authors found for the melting point of cinchonine-d-mandelate 176–177". McKenzie gives 79–80 °. Probably this author interchanged a number of his figures.

Undoubtedly the simplest method of preparing I-mandelic acid is by resolution with I-ephedrine when this base is available. For this purpose 12 g. of 1-ephedrine and 12 g. of dl-mandelic acid are heated together in 40 cc. of 95% alcohol. The crystals obtained on cooling are twice recrystallized from a small volume of alcohol. The optically pure mandelic acid obtained by acidification, extraction with ether and recrystallization by spontaneous evaporation of an acetone solution melted at 133.5° and had $[\alpha]_D^{20°}$ – 156.9° in 2% aqueous solution. The yield was 5.9 g.

Some d-mandelic acid was obtained from the combined mother liquor from which no more crystalline salt was obtainable. The acid after several recrystallizations from water melted at 132°.

Summary

1. A series of bases, structurally similar to ephedrine, has been prepared in order to demonstrate the generality of the reaction described in Paper I.

---

[5] Ing and Manske, J Chem. Soc., 2348 (1926).

[6] McKenzie, J. Chem. Soc , **75,** 966 (1809).

[7] Rimbach, *Ber.,* 32,2385 (1899).

[8] Ward, Chrisman and Nicholas, J. *Chetn. Soc.,* 2186 (1928)

2. Synthetic ephedrine has been resolved into its dextro- and levo-rotatory antipodes, one of which is identical with the base obtained from the Chinese drug, Ma Huang.

3. The resolution was effected by means of d- and *l*-mandelic acid and, conversely, natural I-ephedrine lends itself admirably to the preparation of pure *l*-mandelic acid.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ZION COLLEGE AND OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

PHENYLISOTHIOCYANATE AND ORTHO-TOLYLISOTHIOCYANATE AS REAGENTS FOR PRIMARY AROMATIC AMINES

BY THEO. OTTERBACHER AND FRANK C. WHITMORE

RECEIVED FEBRUARY 19, 1929 PUBLISHED JUNE 5, 1929

Isothiocyanates (mustard oils) react with primary amines to form substituted thioureas suitable for purposes of identification. They are easily crystallized and have convenient melting points. The two isothiocyanates studied in the present work are readily available. They do not react readily with water or alcohol.

The reactions were carried out in alcohol solution. In some cases they took place spontaneously with the evolution of heat, while in others the mixture had to be heated to induce reaction. Since there were no by-products and since the products ciystallized well, they were easily purified to constant melting points by crystallization from alcohol. The yields were almost quantitative.

Phenylhydrazine was also treated with phenylisothiocyanate. It reacted violently with two molecules of the mustard oil.

Hydrazobenzene also reacted with two molecules of mustard oil.

Experimental Part

The substituted thiocarbanilides were prepared by dissolving the calculated amounts of the amine and mustard oil in a convenient quantity of alcohol. From 10 to 50 g. of the amines were used as the thiocarbanilides were desired for another purpose. If no reaction took place in the cold, the contents of the flask were heated to boiling. After gentle boiling for a minute or two, the reaction mixture was allowed to cool. If the product did not separate, even when the wall of the tube was rubbed with a glass rod, the process was repeated until the desired effect was produced. (All of the amines will react in the cold if allowed to stand long enough.) The substituted thiocarbanilide was then filtered off and dissolved in boiling alcohol, filtered while hot and the material separating from the filtrate on cooling was recrystallized again from boiling alcohol. This was usually sufficient to give a sharp melting product. The yields of recrystallized products were 65–80%. The nitrogen content was determined by the Kjeldahl method.

TABLE I

o-TOLYL MUSTARD OIL DERIVATIVES

Amine	Compound	M. p., °C.	Nitrogen, %		Heat required
			Calcd.	Found	
p-Toluidine	$C_{15}H_{16}N_2S$	132	10.9	10.65	
o-Toluidine	$C_{15}H_{16}N_2S$	158	10.9	10.7	
m-Toluidine	$C_{15}H_{16}N_2S$	140	10.9	10.5	–
p-Bromo-aniline	$C_{14}H_{13}N_2SBr$	143	8.7	8.75	+
o-Bromo-aniline	$C_{14}H_{13}N_2SBr$	128	8.7	8.8	+
m-Bromo-aniline	$C_{14}H_{13}N_2SBr$	101	8.7	8.65	+
p-Chloro-aniline	$C_{14}H_{13}N_2SCl$	134.5	10.12	10.2	+
o-Chloro-aniline	$C_{14}H_{13}N_2SCl$	140	10.12	10.2	+
m-Chloro-aniline	$C_{14}H_{13}N_2SCl$	124	10.12	10.2	+
p-Iodo-aniline	$C_{14}H_{13}N_2SI$	150	7.6	7.3	+
3-Bromo-4-amino-toluene	$C_{15}H_{15}N_2SBr$	132	8.3	8.2	+
4-Amino-1,3-dimethylbenzene	$C_{16}H_{18}N_2S$	143.5	10.3	10.2	
2 - Amino - 5 - hydroxytoluene	$C_{15}H_{16}ON_2S$	182.5	10.3	10.3	+
p-Aminophenol	$C_{14}H_{14}ON_2S$	158	10.8	10.7	+
Ammonia	$C_8H_{10}N_2S$	160	16.3	16.71	+
p-Anisidine	$C_{15}H_{16}ON_2S$	138	10.3	10.2	+
o-Anisidine	$C_{15}H_{16}ON_2S$	126	10.3	10.6	+

TABLE II

PHENYL MUSTARD OIL DERIVATIVES

Amine	Compound	M.p., °C.	Nitrogen, %		Heat required
			Calcd.	Found	
p-Toluidine	$C_{14}H_{14}N_2S$	141	11.55	11.6	–
o-Toluidine	$C_{14}H_{14}N_2S$	136	1155	11.65	–
m-Toluidine	$C_{14}H_{14}N_2S$	94	11.55	11.4	–
p-Bromo-aniline	$C_{13}H_{11}N_2SBr$	148	9.1	9.1	+
o-Bromo-aniline	$C_{13}H_{11}N_2SBr$	146	9.1	9.0	+
m-Bromo-aniline	$C_{13}H_{11}N_2SBr$	97	9.1	9.15	+
p-Chloro-aniline	$C_{13}H_{11}N_2SCl$	152	10.6	10.7	+
o-Chloro-aniline	$C_{13}H_{11}N_2SCl$	156	10.6	10 7	+
m-Chloro-aniline	$C_{13}H_{11}N_2SCl$	116	10.6	10.75	+
p-Iodo-aniline	$C_{13}H_{11}N_2SI$	153	7.9	8.0	+
Phenylhydrazine	$C_{20}H_{18}N_4S_2$	172	14.8	14.7	–
Hydrazobenzene	$C_{26}H_{22}N_4S$	168	12.3	12.0	. stand
3-Bromo-4-aminotoluene	$C_{14}H_{13}N_2SBr$	154.5	8.7	8.6	+
4-Amino-1,3-dimethylbenzene	$C_{15}H_{16}N_2S$	133.5	10.93	10.9	–
2-Amino-5-hydroxytoluene	$C_{14}H_{14}ON_2S$	167.5	10.80	10.5	+
p-Aminophenol	$C_{13}H_{12}ON_2S$	150	11.5	11.6	–
Ammonia	$C_7H_8N_2S$	154	18.40	18.3	–

Summary

1. Phenyl mustard oil and o-tolyl mustard oil are satisfactory reagents for many primary aromatic amines, forming well-crystallizing and sharply melting thiocarbanilides in good yields.
2. The reagents do not react with water or alcohol, and a determination may be made in their presence.
3. There are no by-products of the reaction.

ZION, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

SOME UREAS AND THIOUREAS DERIVED FROM VANILLYLAMINE. RELATIONS BETWEEN CONSTITUTION AND TASTE OF PUNGENT PRINCIPLES

BY N. A. LANGE, H. L. EBERT AND L. K. YOUSE

RECEIVED FEBRUARY 20, 1929 PUBLISHED JUNE 5, 1929

Capsaicin, the pungent principle of cayenne pepper, and piperin or chavicin, the pungent principle of black pepper, are both acid amides; capsaicin (I) is the vanillyl amide of A^{6}-8-methylnonenic acid; piperin, δ-piperonylvinylacrylopiperidide, is the piperidine amide of piperic acid; spilanthol, the reduction product of the pungent principle of para-cress is n-decoisobutyl amide.[1]

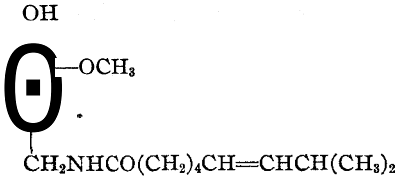
Since these natural pungent principles are acid amides, it is naturally conceivable that a relation might exist between pungency and the amide structure. The synthesis of a number of more or less closely related amides has indeed shown this relation to exist and has also led to conclusions as to the effect on pungency which accompanies changes in the molecular structure. Thus in compounds similar to capsaicin it has been found that a free phenolic group (preferably in the para position to the side chain) in the amine portion is necessary to produce pungency, that the methoxy group in the meta position exerts a favorable influence toward pungency (aromatic bases resembling aniline when replacing the hydroxy benzylamine bases diminish pungency), that the pungency is a maximum when the acid portion consists of nine to ten carbon atoms and that the pungency is not influenced by the position of the double bond in the acid portion. As to the effect of the presence or absence of un-

---

[1] Nelson, THIS JOURNAL, 41,1115 (1919); *ibid.*, 41,2121 (1919); Nelson and Dawson, *ibid.*, 45,2179 (1923); Ott and Eichler, *Ber.*, 55, 2653 (1922); Ott and Lüdemann, ibid., 57,214 (1924); Ott and Zimmermann, *Ann.*, 425,314 (1921); Jones and Pyman, *J Chem. Soc.*, 127, 2588 (1925); Kobayashi, *Rikagaku Kenkyujo Iho*, 4, 527 (1925); Kobayashi, *Inst. Phys. Chem. Research (Tokyo)*, 6,166 (1927); Staudinger and Schneider, *Ber.*, 56, 699 (1923); Staudinger and Miiller, *ibid.*, 56, 711 (1923); Lapworth and Royle, J. *Chem. Soc.*, 115, 1109 (1919); Asahina and Asano, *J. Pharm. Soc. Japan*, 1922, 85.

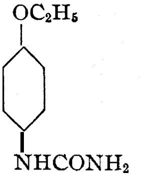
saturation in the acid portion there is still a difference of opinion, some investigators believing that pungency is diminished by the absence of a double bond while others find the saturated derivatives to be equal in pungency to the unsaturated acid derivatives. Capsaicin and closely related substances, aside from the pungent taste, are practically devoid of odor and flavor; dulcin (II) which is the carbamic amide of phenetidine is many times as sweet as cane sugar; studies which have been made on compounds closely related to dulcin have shown that nearly every change in structure causes a lowering or complete loss of sweetness[2] Recently attention has been called to the same effect when one or more of the hydrogen atoms of the nitrogens of the urea are replaced by groups.[3]

Since both capsaicin and dulcin are acid amides derived from an amine having a p-hydroxybenzene structure, it seemed of interest to prepare a series of compounds which would have a rather close similarity to both. As typical of such a condition series of carbamicamides of vanillylamine (III) were prepared and tested particularly for their taste.



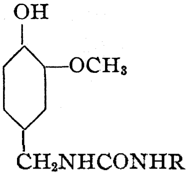
I

Capsaicin, pungent



II

Dulcin, sweet



III

Vanillylamine prepared by the reduction of vanillyl oxime[1] formed the starting product for these syntheses, being converted into the thiourea or urea by treatment with a thiocyanate or cyanate. In this way the following compounds were prepared: vanillylurea, vanillylthiourea, phenylvanillylurea, phenylvanillylthiourea, p-tolylvanillylthiourea and *o*-tolylvanillylthiourea. None of these compounds are sweet but the last three possess pungent properties.

Experimental Part

Preparation of **Vanillylurea (p-Hydroxy-m-methoxybenzylurea),** $(HO)(OCH_3)$-$C_6H_3CH_2NHCONH_2$.—This compound was obtained by mixing **1** mol of vanillylamine hydrochloride with **1.2** mol of potassium cyanate in water solution. Upon standing overnight, light brown crystals of the urea separated and were purified by recrystallizing first from hot water and then from hot alcohol; yield, **90%.** It is fairly soluble in ethyl alcohol, methyl alcohol or water; very slightly soluble in ether, acetone, carbon tetrachloride or chloroform and insoluble in benzene or petroleum ether; m. p. **178.5"** (corr.); it is tasteless in the dry state and in aqueous or alcoholic solutions. The values obtained

---

[2] Boedecker and Rosenbusch, *Ber. pharm. Ges.*, *30*, 251 **(1920);** Speckan, *ibid.*, **32,** 83 **(1922);** Thoms, **Z.** *angew. Chem.*, **37,809 (1924);** Lange and Reed, THIS JOURNAL, **48, 1069 (1926).**

[3] Lorang, *Rec. trav. chim.*, **47,179 (1928).**

on analysis do not agree as closely as they should with the calculated composition; however, repeated attempts at further purification changed neither the analytical values nor the melting point; from the method of preparation we assume that the product was vanillylurea.

Anal. Calcd. for $C_9H_{12}O_3N_2$: C, 55.07; H, 6.17; N, 14.3. Found: C. 55.96, 55.74, 55.96; H, 6.79, 6.74, 6.77; N, 14.0.

Preparation of Vanillylthiourea (p–Hydroxy–m–methoxybenzylthiourea), $(HO)(OCH_3)C_6H_3CH_2NHCSNH_2$.—To 9.5 g. of vanillylamine hydrochloride dissolved in a small volume of water, 5.9 g. of potassium thiocyanate was added. After a few minutes a light brown product began to separate. This solution with its precipitate was evaporated to dryness on a steam-bath and the residue was extracted with boiling water. The vanillylthiourea crystallized from the hot extract. On recrystallizing from water, the solution supercools and no crystals separate until after several hours; a 60% yield was obtained; m. p. 167.5" (corr.). The dry compound as well as the aqueous and alcoholic solutions were tasteless. It is soluble in ethyl alcohol, or methyl alcohol, fairly soluble in water, very slightly soluble in acetone or chloroform and insoluble in ether, carbon tetrachloride, benzene or petroleum ether.

Anal. Calcd. for $C_9H_{12}O_2N_2S$: C, 50.90; H, 5.70. Found: C, 50.28; H, 5.63.

Preparation of Phenylvanillylurea (a–Phenyl–p–p–hydroxy–m–methoxybenzylurea), $C_6H_5NHCONHCH_2C_6H_3(OCH_3)(OH)$.—Vanillylamine base was prepared from the aqueous hydrochloride solution by adding the calculated amount of sodium hydroxide to neutralize the combined hydrochloric acid, shaking and allowing the mixture to stand for several hours, then filtering, washing with cold water and drying in a desiccator; it is easily decomposed by alkalies, boiling water or continued exposure to light. Equimolecular amounts of the base and phenylisocyanate were mixed in a beaker. Heat was evolved and the mixture soon solidified, giving a 63% yield of the urea. Colorless crystals of phenylvanillylurea are obtained by recrystallizing from ethyl alcohol. The compound is fairly soluble in ethyl alcohol, methyl alcohol or acetone, very slightly soluble in ether, chloroform, carbon tetrachloride or benzene and insoluble in water or petroleum ether; m. p. 190.5° (corr.) Solutions of this compound in alcohol are tasteless.

Anal. Calcd. for $C_{15}H_{16}O_3N_2$: C, 66.14; H, 5.93. Found: C, 66.26; H, 5.92.

Preparation of **Phenylvanillylthiourea** (α-Phenyl-β-*p*-hydroxy-*m*-methoxybenzylthiourea), $C_6H_5NHCSNHCH_2C_6H_3(OCH_3)(OH)$.—Five g. of vanillylamine and 4.4 g. of phenylisothiocyanate are mixed; after an initial warming to start the reaction, it proceeds rapidly with an evolution of heat and the formation of a solid mass. The compound was obtained in 92% yield; on treatment with charcoal and recrystallization from alcohol it gave colorless crystals, m. p. 138–138.5° (corr.); it is soluble in acetone, fairly soluble in ethyl alcohol, methyl alcohol or benzene, slightly soluble in chloroform or carbon tetrachloride, very slightly soluble in ether and insoluble in water or petroleum ether. Solutions of the compound in alcohol have a decidedly pungent taste accompanied by a slightly bitter taste

Anal. Calcd for $C_{15}H_{16}O_2N_2S$: C, 62.45; H, 5.60; S, 11.1. Found: C, 62 67; H, 5.57; S, 10.8.

Preparation of ***p*-Tolylvanillylthiourea** (α-*p*-Tolyl-β-*p*-hydroxy-*m*-methoxybenzylthiourea), $CH_3C_6H_4NHCSNHCH_2C_6H_3(OCH_3)(OH)$.—A mixture of 4.6 g. of *p*-tolylisothiocyanate and 4.8 g. of vanillylamine was warmed on a steam-bath for three hours and then recrystallized from alcohol; a 75% yield of *p*-**tolylvanillylthiourea** was obtained; the compound is fairly soluble in ethyl alcohol, methyl alcohol, chloroform, acetone or benzene, very slightly soluble in carbon tetrachloride or ether and insoluble in water or petroleum ether; m. p. 138.5–139° (corr.). Solutions of the compound in alcohol have a decidedly pungent taste accompanied by a slightly bitter taste.

Anal. Calcd. for $C_{16}H_{18}O_2N_2S$: C, 63.53; H, 6.00; S, 10.6 Found: C, 64.04; H, 6.06; S, 10.4.

Preparation of **o-Tolylvanillylthiourea** (α-*o*-Tolyl-β-*p*-hydroxy-*m*-methoxybenzylthiourea), $CH_3C_6H_4NHCSNHCH_2C_6H_3(OCH_3)(OH)$.—Equimolecular quantities of *o*-tolylisothiocyanate and vanillylamine are mixed and then warmed. The compound, obtained in 80% yield, on treatment with charcoal and recrystallization from alcohol gave colorless crystals; m. p. 138–138.5° (corr.); it is soluble in acetone, fairly soluble in ethyl alcohol, methyl alcohol, chloroform or benzene, very slightly soluble in ether or carbon tetrachloride and insoluble in water or petroleum ether. Solutions of the compound in alcohol have a decidedly pungent taste accompanied by a slightly bitter taste.

Anal. Calcd. for $C_{16}H_{18}O_2N_2S$: C, 63.53; H, 6.00; S, 10.6. Found: C, 63.51; H, 5.95; S, 10.7.

Summary

Six different substituted ureas and thioureas have been described; these ureas, being the carbamic or thiocarbamic amides of vanillylamine, are the analogs of the pungent principle of cayenne pepper—a carboxylic amide of the same amine. Three of the thiocarbamides were found to have the property of pungency but to a lesser degree than capsaicin. None of the compounds has a sweet taste, the effect of the phenyl and tolyl groups, which are known to repress the sweetness of compounds, predominating over the favorable effect of the methoxy group; the slightly bitter taste which is characteristic of many thioureas was also observed in several of these compounds.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE ALGINIC ACID FROM MACROCYSTIS PYRIFERA[1,2]

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

RECEIVED FEBRUARY 23, 1929 PUBLISHED JUNE 5, 1929

The earlier researches on the chemistry of the carbohydrates in algae were mostly concerned with the isolation and identification of the sugars formed on the hydrolysis of the plant as a whole. The first attempt at separation of a particular carbohydrate component was made by Stanford[3] and was based on the fact that most marine algae contain a highly polymerized acid fraction which may be extracted by means of dilute alkali

---

[1] Presented before the Organic Chemistry Division of the American Chemical Society at the Swampscott Meeting, September, 1928.

[2] Cf. Cretcher and Nelson, *Science*, 67, 537 (1928), for a preliminary discussion of this subject.

[3] Stanford, *Chem. News*, 47, 254, 267 (1883).

and precipitated by the addition of mineral acid after the removal of the alkali-insoluble residue by filtration.

This substance has been called alginic acid or algin, and in the form of its salts it has a variety of important industrial uses.

Algin was thought by Stanford to contain nitrogen, but later investigations by Krefting,[4] Hoagland and Lieb,[5] as well as our own, have demonstrated that when pure it is nitrogen free. Stanford was apparently interested only in the commercial development of seaweed products, and it was not until 1913 that the algae were again investigated from the standpoint of the original carbohydrate complexes contained in them. Kylin[6] at this time isolated acidic materials from the plants which he later[7] submitted to acid hydrolysis. He reported that the hydrolysis of alginic acid produced apparently only pentoses.

At about the same time, Hoagland and Lieb[5] contributed the results of a careful investigation of the carbohydrates in algae. In the course of their work they prepared alginic acid from the *Macrocystis pyrifera.* After a thorough purification the material was obtained free of more than traces of ash and nitrogen. The neutralization equivalent was found to be 325. Analytical data indicated a compound of formula $C_{21}H_{27}O_{20}$ containing two replaceable hydrogen atoms. It was submitted to acid hydrolysis, the water-insoluble fraction removed by filtration and the filtrate treated with phenylhydrazine. An osazone was isolated having melting point, optical rotation and solubilities in close correspondence to those of the osazone of d-xylose.

Alginic acid, on the basis of these observations, might be considered a compound composed of an unknown acidic nucleus in combination with pentose sugars.

That the acidic nucleus in algin from *Laminaria* is glucuronic acid was recently suggested by Atsuki and Tomoda.[8] The idea that this algin does contain a uronic acid was rendered probable by the fact that their preparation lost 20% of its weight as carbon dioxide when boiled with hydrochloric acid (d. 1.06). No evidence, however, was presented by these authors in proof of the configuration of the acid.

Schmidt and Vocke[9] have hydrolyzed alginic acid from *Fucus serratus* and claim to have isolated, from the hydrolysate, d-glucuronic acid in the form of its cinchonine salt. Proof of the identity of this salt is limited to the determination of its melting point and is inconclusive.

The present authors are of the opinion that Schmidt and Vocke's method

[4] Krefting, English Patents, 11,583 (1896); 12,416 (1898).

[5] Hoagland and Lieb, *J Biol. Chem*, 23,287 (1915).

[6] Kylin, *Z. physiol. Chem.*, 83,171 (1913).

[7] Kylin, *ibid.*, 94,337 (1915).

[8] Atsuki and Tomoda, *J. Soc. Chem. Ind. (Japan)*, *29,* 509 (1926).

[9] Schmidt and Vocke, *Ber.*, 59, 1585 (1926).

of hydrolysis does not completely liberate the monomolecular uronic acids from their polymers and the cinchonine salt which they prepared and which melted at 204° was not of a simple C_6 aldehyde sugar acid. We have submitted the algin from Fucus serratus to more drastic hydrolysis and have obtained from the product a cinchonine salt melting at 152°. This is the melting point of the cinchonine salt of the C_6 aldehyde acid which we have isolated from Macrocystis *pyrifera*. The two acids are probably identical and are surely not glucuronic. It is to be admitted, however, that more than one uronic acid may be present in Fucus serratus.

We have isolated the alginic acid from Fucus serratus, *Laminaria* agardhii and Macrocystis *pyrifera*.[10]

In the case of the first mentioned algin, no analytical work has been done on the original material. The algins from the *Laminaria* agardhii and Macrocystis have, however, been studied analytically. These acids, free of more than traces of ash and nitrogen, were dried over phosphorus pentoxide to constant weight. They gave strong naphtho-resorcin tests and were therefore thought to contain uronic acids. Titration with standard alkali gave neutralization equivalents varying, with different samples, from **176** to **184.** Carbon and hydrogen determinations indicated the formula $(C_6H_8O_6)_n$, while boiling with hydrochloric acid caused the liberation of carbon dioxide to the extent of 24–25%. The pure acids do not reduce Fehling's solution. These facts indicate that algin is a polyuronic acid in which all carboxyl groups are free and all aldehyde groups conjugated.

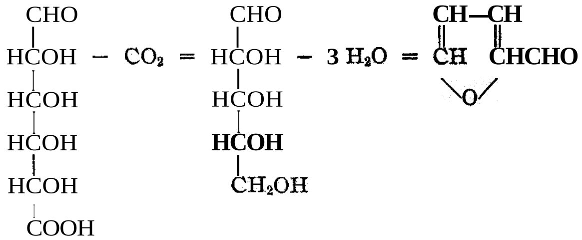
But little study beyond the determination of the analytical data has been made of the algin from Laminaria agardhii. That from Macrocystis *pyrifera* has been hydrolyzed to the free C_6 aldehyde acid, which was not obtained in crystalline condition. It did not have the properties of either d-galacturonic or d-glucuronic acid. These are the only aldehyde sugar acids which have been found in nature to date. That it was neither a mixture of these acids nor either of them in impure form was indicated by the fact that neither mucic nor saccharic acid could be isolated after oxidation with bromine or nitric acid and that the pure cinchonine salt of the aldehyde acid did not have properties in correspondence with those of the galacturonic or glucuronic salts of this alkaloid.

It was shown by Salkowski and Neuberg[11] that glucuronic acid may be converted, by bacteria, into d-xylose. It is also well known that uronic acids lose carbon dioxide on treatment with hot aqueous mineral acids and that furfural is a product. It may be assumed that a pentose sugar is intermediate in this process and that the reaction is as follows:

---

[10] Further investigation of *Fucus serratus* is now under way in this Laboratory and will be reported soon.

[11] Salkowski and Neuberg, Z. *physiol. Chem.,* 36, 261 (1902); 37, 464 (1903).



This would explain the formation of the pentoses which were reported by Kylin[7] and by Hoagland and Lieb.[5]

If the osazone isolated by the last mentioned investigators was actually that of d-xylose, it is identical with the osazone of the epimer of d-xylose, namely, d-lyxose. The identification of the uronic acid was thus simplified somewhat, inasmuch as it must be of such configuration as to form either d-xylose or d-lyxose on loss of carbon dioxide. A consideration of the conventional stereochemical formulas of the hexoses will reveal that of the sixteen possible hexuronic acids, only four can meet this condition. d-Glucuronic and *l*-iduronic would form d-xylose; d-mannuronic and l-guluronic would form d-lyxose. Glucuronic was excluded by experiment. Iduronic and guluronic being derivatives of sugars not as yet found in nature were thought improbable. Inasmuch as *d*-mannose is widely distributed in nature, and as we found mannitol in the Macrocystis to the extent of 4–5%, we assumed, as a working hypothesis, that the algin contained d-mannuronic acid. Evidence in support of this hypothesis is given in the Experimental Part.

Experimental Part

Isolation of **Mannitol** from Macrocystis **Pyrifera.**—One hundred and fifty grams of air-dried fronds were extracted by boiling in 1000 cc. of alcohol. After filtering, the fronds were extracted again with 500 cc. of alcohol. After filtering and washing with alcohol, the filtrate was evaporated to a small volume. During the evaporation, colorless needles separated from solution. The solution was filtered and the solid washed with alcohol. After once recrystallizing, the compound melted at 166°. The melting point of mannitol as determined by Landolt[12] is 166°. It was converted into a tribenzal compound according to the method of Fischer. The compound melted at 218–222° (corr.), the temperature of melting of tribenzalmannitol as determined by Fischer and Fay.[13]

Preparation of **Alginic** Acid from Macrocystis.—The air-dried fronds containing 18% moisture and 25.5% ash were washed several times with water and allowed to stand completely immersed in 0.5% hydrochloric acid for twenty-four hours. The acid was decanted and the process twice repeated. After again washing thoroughly with water, the leaves were covered with 2% sodium carbonate solution. and allowed to stand overnight. Almost immediately on addition of the alkali the fronds swell, lose their shape and the solution becomes very viscous. Frequent stirring facilitates the

---

[12] Landolt, *Z. physik. Chem.*, 4, 366 (1889).

[13] Fischer and Fay, *Ber.*, 28, 1975 (1895).

extraction of the alginic acid. The solution was diluted to the point where it could be filtered through a medium finely woven scrim without suction. The residue was extracted again with 2% sodium carbonate and filtered.

The combined filtrate was warmed to 60° and filtered, under suction, through a thin layer of decolorizing carbon on a coarse filter paper. After the solution had cooled to room temperature, the alginic acid was precipitated by the addition of hydrochloric acid under vigorous stirring. The precipitated acid was filtered on scrim and allowed to drain as dry as possible. It was then washed with water, transferred to a large crock, allowed to stand overnight under a large volume of 0.5% hydrochloric acid and filtered. This process of extraction with dilute acid is for the purpose of removing both ash and acid soluble nitrogen compounds. It was repeated thrice. The hydrochloric acid was then removed by several similar treatments with distilled water.

The alginic acid so prepared is a very highly hydrated gel from which water cannot be removed by centrifugation or filtration.

In order to effect dehydration, the gel was treated with 95% alcohol and allowed to stand overnight. This treatment also extracts a considerable amount of alcohol-soluble brown pigment. The alcohol and most of the water were then removed from the alginic acid by means of a hydraulic press and the alcohol extraction repeated. After pressing the second time, a hard cake was obtained. This was broken into small pieces and allowed to dry in the air and finally, in *vacuo,* over phosphorus pentoxide. The yield of purified algin obtained was about 15% of the weight of the fronds taken.

Properties of Alginic Acid.—The most striking physical property of alginic acid is its remarkable power of adsorption of water and salts. Hoagland and Lieb[5] state that "it is capable of adsorbing 200 to 300 times its weight of water" and "salts to the extent of 60%." While we have made no attempt to discover the upper limit of water absorption, we can state that when free of salts and mineral acid the water adsorbed may be considerably higher than 200%. Only by repeated dialysis with dilute acid can the ash be reduced to 0.1%, which gives the purest sample we have been able to prepare. The ash remaining after careful purification is composed largely of iron.

Alginic acid is very slightly soluble in water. It liberates carbon dioxide from carbonates and may be titrated with alkali to a definite end-point (phenolphthalein). It does not reduce Fehling's solution but rapidly forms reducing substances if dried at 100° or if boiled with water or dilute acid. Considerable amounts of carbon dioxide are liberated under the same conditions. Because of this sensitivity of alginic acid, its optical rotation and acid value vary with the time and temperature of drying. This important fact has apparently escaped the observation of previous investigators. The optical rotation of sodium alginate prepared from the alginic acid of the *Macrocystis pyrifera* is $[\alpha]_D^{20} = -133°$.

Analysis of Alginic Acid

Titration *with* **Alkali.**—0.3035 g. of sample required 16.93 cc. of 0.1 *N* NaOH, corresponding to a neutralization equivalent of 179.

Uronic Acid **Carbon** Dioxide.—On boiling a sample of alginic acid for five hours with 12% hydrochloric acid, it lost 21.5% of its weight as carbon dioxide. This corresponds to 86% of uronic anhydride. The neutralization equivalent, however, indicated almost 100%. A sample was therefore boiled with 18% hydrochloric acid. After five hours 0.5519 g. lost 0.1462 g. of carbon dioxide. Calcd. for $C_6H_8O_6$: CO_2, 25. Found: CO_2, 24.65.

Carbon and Hydrogen.—Calcd. for $C_6H_8O_6$: C, 40.91; H, 4.55. Found: C, 41.21; H, 4.75.

Hydrolysis of Alginic Acid.—Hydrolysis was first attempted by boiling with distilled water. After boiling for a short time, water-soluble reducing substances were formed. It was thought that the progress of the hydrolysis could be followed by determination of the ratio of aldehyde to carboxyl by titration. A polyuronic acid would theoretically be completely degraded to C_6 aldehyde acid when this ratio became 1:1. After ninety hours' heating, this ratio was obtained. The aldehyde was determined by the iodine titration method of Wiilstatter and Schudel[14] and the carboxyl by standard alkali. On attempting to isolate the free uronic acid, it was found that the product of the hydrolysis was a substance containing too little aldehyde for the uronic acid and that the apparent formation of a uronic acid was the result of a slow increase of aldehyde from hydrolysis and a gradual loss of carbon dioxide from the carboxyl groups.

During this process the hydrolysis and loss of carbon dioxide is quite rapid at first but becomes very slow after some hours. Even after prolonged hydrolysis, a water-insoluble residue of polyuronic acid remains. Apparently the loss of carbon dioxide is coincident with or follows the hydrolysis, as the water-insoluble residue was shown by analysis to be 100% polyuronic anhydride.

A sample of alginic acid was shown, by experiment, to lose 10% of the theoretical amount of carbon dioxide on boiling with distilled water for eighteen hours.

An air-dried sample of alginic acid containing 17% of moisture lost 0.82% *(dry* basis) of its carbon dioxide when dried at 100° for four and one-half hours.

Hydrolysis with Dilute Sulfuric Acid.—Hydrolysis with dilute sulfuric acid of various concentrations was attempted but soon abandoned because of the simultaneous loss of carbon dioxide.

It seems worthy of mentioo that we obtained, after hydrolysis with water for forty-two hours and then with 3% sulfuric acid for an additional five hours, a residue which was still a polyuronic acid. This residue was separated from the solution by centrifugation, was washed with water and alcohol, dried over phosphorus pentoxide and analyzed for aldehyde and uronic acid carbon dioxide. Its neutralization equivalent was 180. The carbon dioxide determination corresponded to 99.6% uronic anhydride, while the titration of aldehyde indicated a polyuronic acid, $C_{72}H_{98}O_{73}$, containing one free aldehyde and twelve carboxyl groups. The stability of this residue as to loss of carbon dioxide and its comparatively high resistance to hydrolysis indicate that the uronic acids in algin are not all similarly conjugated.

Hydrolysis with Nitric Acid.—It was thought that by treatment with nitric acid it might be possible, simultaneously, to hydrolyze and oxidize the aldehyde acid formed to a dibasic acid. At 55° with nitric acid of sp. gr. 1.2 the main product was oxalic acid. A water-insoluble residue was again obtained.

Hydrolysis with 80% Sulfuric Acid.—The hydrolysis of alginic acid was best accomplished in the following manner: 30 g. of the dry pulverized acid was thoroughly mixed with 90 g. of cold 80% sulfuric acid. The flask was stoppered and allowed to stand for five days at room temperature. The contents was then slowly poured into 900 cc. of water. The water-insoluble residue was removed by filtration and

---

[14] Willstätter and Schudel, *Ber.*, 51,780 (1918).

washed with water and alcohol. This residue was a polyuronic acid and weighed 6 g. This substance is now being studied but will not be discussed further in this communication.

The filtrate was heated to the boiling point and treated with the calculated amount of barium carbonate to remove the sulfuric acid. The barium sulfate was filtered off and washed with hot water. The combined filtrate and washings was treated with barium carbonate, with stirring, and heated over a water-bath for two hours after the solution had become neutral to Congo Red. Long heating is necessary*to convert the lactone of the aldehyde acid to the barium salt. The excess barium carbonate was removed by filtration and the filtrate evaporated under reduced pressure to 100 cc. The solution was allowed to stand in the ice box overnight. The small amount of dark brown precipitate formed was filtered off and discarded. The solution was treated with decolorizing carbon (Nuchar), filtered and evaporated, in *vacuo,* to 25 cc.; 100 cc. of 95% alcohol was added. The barium salt was precipitated as a heavy gum. After standing in the ice box for several hours, the supernatant liquor was removed by decantation. The gum was dried at 35–40" until it could be powdered. The yield of dry salt was 25 g. Analysis of this salt proved it to be mostly the barium salt of a C_6 aldehyde sugar acid, with small amounts of lactone and the barium salts of polyuronic acids which had escaped hydrolysis. No method was discovered for complete purification of this salt. On removal of the barium with sulfuric acid and evaporation of the solution, a sirup was obtained which we did not succeed in crystallizing.

Addition of excess barium hydroxide to a solution of the aldehyde acid causes the precipitation of a practically insoluble basic salt.

The Cinchonine Salt.—Inasmuch as the cinchonine salts of glucuronic and galacturonic acids have been described, a solution of the uronic acid was treated with cinchonine in the manner usual for the preparation of alkaloidal salts. The excess cinchonine was extracted with chloroform and the solution evaporated to a small volume. The cinchonine salt is quite soluble in water and separates, even from highly supersaturated solutions, very slowly. It was recrystallized from water to constant melting point and then once from alcohol. The alcohol crystallization did not alter the melting point, which was 152° corr. Melting is accompanied by effervescence.

Anal. Calcd. for $C_{25}H_{32}O_8N_2$: N, 5.72. Found: N, 5.95; 5.58. 0.2451 g. was dissolved in water and the cinchonine precipitated by addition of 5 cc. of $0.1N$ NaOH and filtered off. The filtrate was titrated for aldehyde. Calcd. for $C_{25}H_{32}O_8N_2$: 0.1 N iodine required, 10 cc. Found: 9.6 cc. Optical rotation. 0.3016 g. in 25 cc. of H_2O in a 2-decimeter tube gave an observed rotation of $+2.74°$; $[\alpha]^{25}_{D} = +113.6°$.

The physical constants of the cinchonine salts of *d*-glucuronic and d-galacturonic acids given in the literature are as follows: glucuronic, m. p. 204°,[15] 199–200°;[16] *[a]*= 138.6°,[15] 135°,[16] 139.9°;[17] galacturonic, m. p. 158°;[17] *la]* = 134°.[17]

Oxidation of the Aldehyde Acid.—Inasmuch as many of the dicarboxylic sugar acids are known and some of them are quite well characterized, it was thought that our unknown uronic acid could best be identified by oxidation to a dibasic acid. The method of oxidation was as follows:[18] 8 g. of the barium salt of the aldehyde acid was

---

[15] Neuberg, Ber., **33,** 3317 (1899).

[16] Ehrlich and Rehorst, ibid., 58, 1989 (3 925).

[17] Schwalbe, ibid., 58, 1536 (1925).

[18] This method of oxidizing an aldose by bromine water in the presence of a buffering salt such as barium benzoate was suggested to us by C. S. Hudson. An article fully describing the method and its application to various sugars will be published in the near future by C. S Hudson and H. S. Isbell.

dissolved in **250** cc. of water, **12** g. of barium benzoate and 5 cc. of bromine were added and the solution was allowed to stand at room temperature for three days. The excess bromine was removed by blowing a rapid stream of air through the solution and the precipitated benzoic acid removed by filtration. The solution was next extracted with chloroform to remove the dissolved benzoic acid.

Barium carbonate was added, with heating and vigorous stirring. It was heated for one and a half hours after the solution became neutral to Congo Red. It was then treated with decolorizing carbon and filtered. The filtrate was evaporated to **70** cc. under reduced pressure. On cooling, a small amount of brown material precipitated and was removed by filtration. The filtrate was poured into two volumes of alcohol. The solid barium salt was filtered off and ground under 50% alcohol. It was then filtered and washed with alcohol of the same strength. Barium was removed from the salt by sulfuric acid. After filtration the solution was evaporated to a sirup, which was treated with absolute alcohol. This precipitated traces of salts and a small amount of sticky carbohydrate material. The alcoholic solution was filtered and evaporated to a sirup which could not be induced to crystallize, even after samples of it were seeded with a crystal of d-mannosaccharic dilactone or mucic acid. A sample was neutralized with **50%** potassium hydroxide and then acidified with acetic acid but no potassium acid saccharate could be isolated from the reaction product.

The **Diamide.**—A sample of the sirup was treated with an excess of concentrated ammonia. On standing for some hours in the ice box a white crystalline compound was deposited. It was filtered off and washed with cold water, then with alcohol and finally with ether. It was recrystallized from hot water to constant melting point and rotation.

Anal. Calcd. for $C_6H_{12}O_6N_2$: N, **13.46.** Found: **N, 13.35.**

The compound melted at 189° with decomposition. A mixed melting point with d-mannosaccharic diamide was **189°.** The melting point of mannosaccharic diamide was found to be 189° by Fischer[19] and **188–189.5'** by Hudson.[20] **Our** sample of this diamide prepared from mannose melted at **189°**.

0.1552 g. of the diamide, prepared from algin according to methods already described, in **50** cc. of water, gave or $=$ **$-0.304'$** in a **4-dm.** tube, as an average of eight readings; $[\alpha]^{20}_{D} = -24.46°$. The rotation of *d*-mannosaccharic diamide, as determined by Hudson,[20] is $[\alpha]^{20}_{D} = -24.4°$.

The **Di-phenylhydrazide.**—A sample of the sirup was heated on a water-bath with an excess of phenylhydrazine acetate. The di-phenylhydrazide formed was very insoluble in hot water or alcohol. It was extracted once with boiling water and thrice with hot alcohol. It melted with decomposition at **212°**.

d-Mannosaccharic di-phenylhydrazide was prepared from pure crystalline *d*-mannosaccharic dilactone. It melted at 212°. This is also the melting point reported by Fischer.[19] A mixture of the two hydrazides melted at the same temperature.

Our thanks are due to Thornley and Company of San Diego, California, for their kindness in supplying us with the fronds of *Macrocystis pyrifera.*

Summary

1. Pure alginic acid has been prepared from the *Macrocystis pyrifera* and shown to be a polymer of the anhydride of an aldehyde sugar acid in which all aldehyde groups are conjugated and all carboxyl groups free.

---

[19] Fischer, *Ber.*, **24,539 (1891).**

[20] Hudson, THIS JOURNAL, **41, 1141 (1919).**

2. The uronic acid has not been obtained in crystalline condition. It may be oxidized to a dibasic C_6 sugar acid. The diamide and diphenylhydrazide of this acid correspond in properties to the analogous compounds prepared from pure d-mannosaccharic dilactone.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

TIN TETRAPHENYL AS A PHENYLATING REAGENT

BY R. W. BOST AND P. BORGSTROM

RECEIVED FEBRUARY 25, 1929 PUBLISHED JUNE 5, 1929

Certain of the organo-metallic compounds have been used as phenylating reagents. Mercury[1] and magnesium diphenyl[2] have been used to introduce the phenyl groups into certain compounds. Aryl tin halides were first made by the reaction of mercury diphenyl and stannic chloride.[3] Later the reaction between tin tetraphenyl and halogens to form mono-, di and triaryl halides has been carefully studied.[4] More recently Goddard and his co-workers[5] have isolated products from tin tetraphenyl and thallic chloride, while no derivatives were obtainable with the chlorides of mercury and sulfur with tin tetraphenyl.

Since tin tetraphenyl is comparatively rich in phenyl groups, and since its toxicity is much lower than that of mercury diphenyl, it seemed desirable to study the possibilities of using it as a reagent for introducing the phenyl group into organic compounds. In this paper are presented the reactions of tin tetraphenyl with the following types of compounds: halogens, alkyl halides, acyl halides, sulfur, nitric acid and sulfuryl chloride.

Experimental Part

1. Action of Halogens.—Bromine and chlorine react violently with tin tetraphenyl. Even at 0° they react energetically to give excellent yields of the corresponding monohalides of benzene. The reaction using iodine is less active and low yields of phenyl iodide are obtained. Iodine monochloride reacts very readily and produces a good yield of phenyl iodide. No halogen disubstitution products of benzene were detected under the conditions of the experiment.

Bromobenzene.—Twelve and seven-tenths grams of bromine was slowly added with a dropping funnel to 8.5 g of tin tetraphenyl in a round-bottomed flask connected with a reflux condenser, the flask being cooled in an ice–salt mixture. The bromine was rapidly taken up, forming a colorless liquid, until most of the bromine had been

---

[1] Dreher and Otto, Ann., 154, 97 (1870).

[2] Waga, *ibid.*, 282,323 (1894).

[3] Aronheim, *ibid.*, 194, 145 (1878).

[4] Polis, Ber., 22,2918 (1899); Krause, ibid., 51,912 (1918); Chambers and Scherer, THIS JOURNAL, 48, 1055 (1926).

[5] Goddard and Goddard, J. *Chem. Soc.*, 121, 256 (1922); Goddard, Ashley and Evans, *ibid.*, 121,978 (1922).

added. Much heat was evolved in the reaction. After all of the bromine had been added, the reaction mixture was heated on a steam-bath for one hour. The phenyl bromide was removed by distillation, then washed, dried and redistilled. The fraction boiling from 154–156° was collected; yield, 94%.

Chlorobenzene.—To 8.5 g. of tin tetraphenyl in a cooled flask as above described was slowly added 5.7 g. of chlorine dissolved in carbon tetrachloride. A vigorous reaction took place, evolving much heat. After all of the chlorine had been added, the mixture was heated for thirty minutes on the steam-bath. The chlorobenzene was distilled off, washed, dried and the fraction boiling between 131–133" was reserved; yield, 91%.

Iodobenzene.—An apparatus similar to the one in the above experiments was used; 13 g. of iodine monochloride dissolved in 200 ml. of carbon tetrachloride was slowly added to 8.5 g. of tin tetraphenyl in a flask cooled with ice. The addition required about twenty minutes. The mixture was refluxed for four hours and set aside for twenty-four hours. The carbon tetrachloride was distilled from the steam-bath, and then the crude iodobenzene. The phenyl iodide was washed, dried and the fraction 187–188° reserved; yield, 74%.

2. Action of Alkyi Halides.—Certain alkyl halides were heated with tin tetraphenyl but poor results were obtained with this group of compounds. There seems to be a tendency for the alkyl halides to split off halogen acids, giving an unsaturated hydrocarbon, the triaryl tin halide and some unused tin tetraphenyl. This is true with *iso*-amyl bromide and to a certain extent with *tert.*-butyl bromide. Chloroform and bromoform gave no apparent reaction under ordinary conditions. The former in a sealed tube gave mostly triphenyl tin chloride.

***Tert.*-Butylbenzene.**—A mixture of 8.5 g. of tin tetraphenyl and 12 g. of *tert.*-butyl bromide was heated under reflux for eighteen hours. As the reaction proceeded the solution after first darkening became light in color The reaction product was filtered, excess of *tert.*-butyl bromide distilled off and the *tert.*-butylbenzene distilled under reduced pressure; yield, 8%. An unsaturated hydrocarbon, a halogen acid and the aryl tin halide were also formed.

Reaction with Iso-amyl Bromide.—Eight and five-tenths grams of tin tetraphenyl and 13 g. of iso-amyl bromide were refluxed for twenty hours. The reaction product gradually darkened. The presence of a halogen acid, an unsaturated hydrocarbon and the aryl tin halide were detected but the main product was unchanged tin tetraphenyl and iso-amyl bromide. No iso-amylbenzene was observed.

Reaction with Chloroform.—Twelve and seven-tenths grams of tin tetraphenyl and 4.7 g. of chloroform were heated in a sealed tube at 260° for twenty hours. The brownish-yellow residue was washed from the tube with ether and filtered. The insoluble portion consisted mainly of unused tin tetraphenyl The filtrate after being decolorized with charcoal yielded three grams of triphenyl tin chloride and traces of triphenylmethane.

3. Action of Acyl Halides.—The reaction between tin tetraphenyl and acetyl chloride, benzoyl chloride, and benzene sulfonyl chloride to form ketones was very slow under ordinary conditions. Only traces of phenyl ketones were obtained when boiled under reflux. High temperatures and pressures were necessary to produce an appreciable yield and even then the yield was poor in the case of acetyl chloride.

Acetophenone.—Eight and five-tenths g. of tin tetraphenyl and 10 g. of acetyl chloride were heated in a sealed tube at 100° for fifteen hours. A dark oil was obtained. This was filtered and the filtrate was washed, dried and distilled. After two fractionations a light yellow oil was obtained which boiled at 200–205°; yield of acetophenane, 1 g.

Benzophenone.—Eight and five-tenths g. of tin tetraphenyl and 12.5 g. of benzoyl chloride were heated in a sealed tube at 200° for ten hours. The reaction product was washed from the tube with ether and filtered. The ether was evaporated and the brownish oil repeatedly washed with hot water to destroy any unused benzoyl chloride. The brownish liquid partially solidified. It was transferred to a distilling flask and the portion coming over from 297 to 305° was reserved; crude yield, 7%; redistilled and recrystallized from alcohol, m. p. 48°.

Diphenylsulfone.—Eight and five-tenths g. of tin tetraphenyl and 14.1 g. of benzenesulfonyl chloride were heated in a sealed tube at 200° for eighteen hours. The dark viscous product in the tube was rinsed out with benzene and filtered. The filtrate yielded 34% of crude diphenylsulfone The crude produc was purified from hot water; m. p. 122–124°.

4. Action of Sulfur.—Reactions between tin tetraphenyl and sulfur were carried out under different conditions of time, temperature and concentrations of sulfur. As the temperature was increased the products changed from diphenyl sulfide to diphenyl disulfide and to thianthrene, using more sulfur for the second and third than for the first. It is necessary to carry out the reactions in a sealed tube to get the best results.

Diphenyl Sulfide.—Eight and five-tenths g. of tin tetraphenyl and 1.9 g. of flowers of sulfur (three atomic weights) were heated in a sealed tube at 170° for ten hours. The reaction product was a golden yellow liquid. The product was filtered and distilled. About two grams of benzene was obtained as a by-product. The diphenyl sulfide boiled at 295–297°; yield, 76%.

Diphenyl **Disulfide.**—Eight and five-tenths g. of tin tetraphenyl and **3.2** g. (five atomic weights) of sulfur were heated in a sealed tube at 190" for eight hours. The reaction product consisted of a brownish-yellow solid. This was extracted with hot ether, which upon evaporation and distillation yielded two grams of diphenyl sulfide and 4.8 g. of diphenyl disulfide (m. p. 60°).

Thianthrene.—Eight and five-tenths g. of tin tetraphenyl and 3.2 g. (five atomic weights) of sulfur were heated in a sealed tube at 250° for twenty hours. Hydrogen sulfide was given off when the tube was opened. The brownish-yellow product was extracted with ether and filtered. It was only slightly soluble in ether. It was then extracted with hot absolute alcohol and filtered From the filtrates were isolated 2 g. of phenyl sulfide, less than 1 g. of diphenyl disulfide and about 2 g. of thianthrene (m. p. 155–158°).[6]

5. Action with Nitric Acid.—To 8.5 g. of tin tetraphenyl in a flask cooled with an ice–salt mixture and fitted with a reflux condenser, was slowly added 5 ml. of concentrated nitric acid. At first only a gentle reaction occurred. Soon a violent reaction was set up. After the reaction had ceased the product was heated on a steam-bath for thirty minutes. The product was then washed, dried and distilled. The fraction boiling at 208–210° was reserved; yield, 2 g. Whether the nitrobenzene was formed when the tin tetraphenyl was decomposed or whether benzene was first formed and then nitrated is not known from these experiments.

6. Action of **Sulfuryl** Chloride.—From the product of refluxing 8.5 g. of tin tetraphenyl with 5.4 g. of sulfuryl chloride in benzene were isolated only unchanged tin tetraphenyl and a small amount of triphenyl tin chloride (m. p. 105–106°). When 8.5 g. of tin tetraphenyl and 20 ml. of sulfuryl chloride (without solvent) were refluxed, sulfur dioxide was evolved and only a small amount of diphenyl tin hydroxychloride (m. p. 184–185°) was identified. What the course of this reaction is and what other products are formed need further study.

---

[6] In all cases the compound isolated whose melting point or boiling point is given was checked by mixing with the same compound from another source and again determining the constant.

Summary

1. Tin tetraphenyl reacts with (*a*) halogens to form aryl mono halides, (b) acyl halides to form phenyl ketones, ***(c)*** sulfur to form diphenyl sulfide, diphenyl disulfide and thianthrene. The reactions with alkyl halides and sulfuryl chloride were not conclusive. With nitric acid nitrobenzene was isolated.

CHAPEL HILL, NORTH CAROLINA
WASHINGTON, D. C.

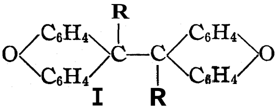
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. V. THE RATE OF DISSOCIATION[1]

BY JAMES B. CONANT AND MILDRED W. EVANS[1]

RECEIVED FEBRUARY 28, 1929 PUBLISHED JUNE 5, 1929

More than a dozen derivatives of dixanthyl of the type represented by Formula I have been prepared and studied in this Laboratory.[2]



I (R = an alkyl or aryl group)

All of them in solution absorb oxygen at room temperature and in many cases the reaction is so rapid that the speed of the process is limited only by the rate of solution of the gas. However, those compounds in which the substituting group may be represented as RCH_2CH_2— are much less rapid in their action and it is possible, therefore, to study their auto-oxidation at room temperature. A few approximate measurements of the rate of oxidation of these substances were made in connection with their preparation; these results have been reported in the previous papers of this series. In order to learn more about the nature of the reaction, we have now undertaken a more detailed study of the auto-oxidation of a typical representative of the class, di-n-butyldixanthyl. The results of this investigation, which we are about to describe, led to the unexpected conclusion that we were in reality measuring a rate of dissociation into free radicals. Since the relation between this rate and the tendency of the compound to dissociate on heating is a matter of great interest, we continued the work and included a study of a number of homologs of di-*n*-butyldixanthyl at different temperatures. A discussion of the results so obtained forms the concluding portion of this paper.

In the case of many compounds which are appreciably dissociated in

---

[1] This paper is part of a thesis presented by Mildred W. Evans at Radcliffe College for the degree of Doctor of Philosophy.

[2] Conant and co-workers, THIS JOURNAL, 47, **572,** 3068 **(1925); 48, 1743 (1926); 49,2080 (1927).**

solution below 100°, the reaction with oxygen at 25° (in solution) proceeds almost quantitatively according to the reaction

$$R_3C—CR_3 + O_2 \longrightarrow R_3C—O—O—CR_3$$

The maximum amount of oxygen absorbed is one mole per mole of substance and a crystalline peroxide may be isolated in amounts as large as 80% of the theoretical. Such is the case, for example, with dibenzyldixanthyl, which absorbs oxygen very rapidly in solution. There seems to be no reason to believe that there is any fundamental difference between such a reaction and the slower oxygen absorptions of such compounds as di-n-butyldixanthyl. Indeed, it is possible to isolate the peroxide in this case, also, although the yield is poor. There is, however, another side reaction involving further oxidation of the peroxide or some intermediate oxide, since the total amount of oxygen absorbed corresponds to more than one mole. In the case of some of the alkyl dixanthyls as much as 2.5 moles of oxygen can be absorbed by prolonged exposure of the solution to oxygen. The susceptibility of the first oxidation product to further oxidation obviously accounts both for the low yields of peroxide and the increased oxygen consumption. We may, therefore, regard the measured rate of oxygen absorption of di-*n*-butyldixanthyl as the sum of the relatively fast normal reaction and a slower secondary oxidation which becomes appreciable only after the reaction has proceeded for some time. This is illustrated in Fig. 1, in which the rate of oxygen absorption of di-n-butyldixanthyl over a long period of time was measured (Curve A). For the first half mole of oxygen absorbed this curve corresponds to that of a monomolecular reaction (Curve B). Assuming this to be the major reaction, the Curve C represents the slower side reaction which is responsible for the diminution in yield of peroxide.

We have centered our attention on a study of the rate of the oxygen absorption in that range (0 to 0.6 of a mole of oxygen) in which the side reaction mentioned above appears to be negligible. We have calculated the fraction of dixanthyl derivative which has reacted at any given time from the volume of oxygen absorbed at that time and the calculated volume corresponding to 100% peroxide formation. This procedure introduces no error in the range in which the side reaction is negligible.

In Table I are collected representative measurements from our preliminary study of the factors affecting the speed of the reaction. The differential pressure apparatus employed was that described in detail later in this paper. At the time these measurements were made the experimental error was of the order of 10%, although later experiments reduced this to about **3%.** The di-n-butyldixanthyl was dissolved in bromobenzene and the solution shaken with a large excess of air or oxygen. The volume of oxygen absorbed was calculated from the change in pressure. The concentration of dissolved oxygen throughout a given experiment was constant and therefore if the reaction were bimolecular, of the type $A + O_2 \longrightarrow AO_2$, the rate would nevertheless correspond to a first-order reaction. However, if the composition of the gaseous phase is changed, the concentration of dissolved oxygen must change. Thus, if the rate-controlling step involved the interaction of oxygen and the organic molecule, the rate should increase about five-fold on changing from air to oxygen. Actually there was no change (compare 1 and 2, 3 and 4, 5 and 6, in Table I). This fact shows that the combination with oxygen must be relatively fast and that

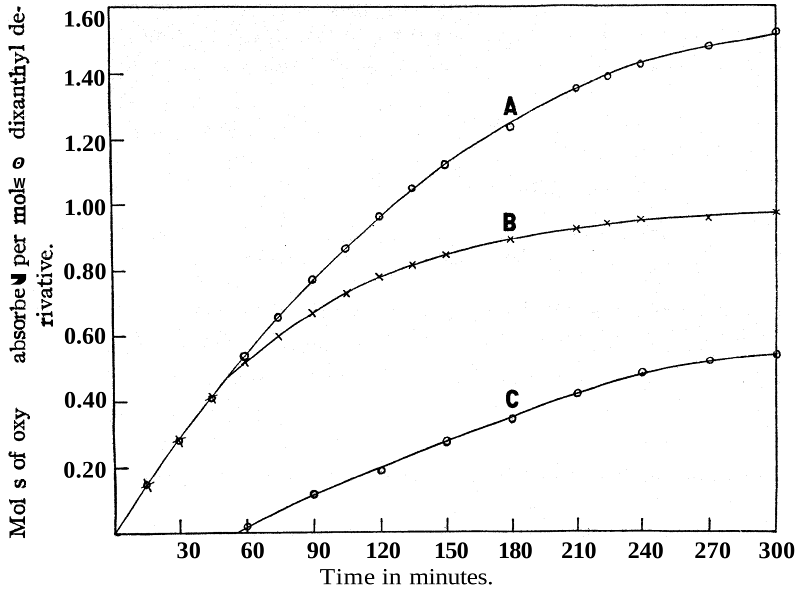


Fig. 1.—Rate of oxygen absorption of dibutyldixanthyl at 25° in bromobenzene solution. Curve A, observed rate; Curve B, calculated from first-order equation to correspond with A during first part of reaction; Curve C, difference between A and B.

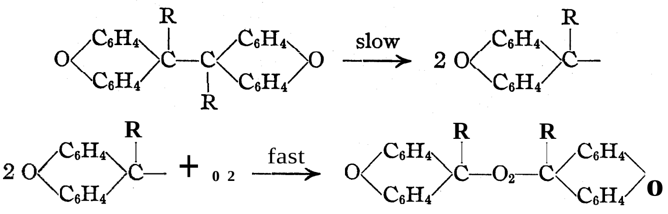
TABLE I

THE RATE OF OXYGEN ABSORPTION OF DI-*n*-BUTYLDIXANTHYL

Expt.	Temp., °C.	Gas	Concn. of dixanthyl deriv., M	Fraction of dixanthvl derivative reacted in 10 min.	15 min.	20 min.	30 min.	45 min.	Remarks
1	15	Air	0.01	...	0.10	...	0.13	0.15	0.29 at 2 hrs.
2	15	Oxygen	.01	...	.05	...	.12	.14	.28 at 2 hrs.
3	25	Air	.01	0.09	.13	0.17	.23		
4	25	Oxygen	.01	.11	.14	.17	.26		
5	25	Air	.01	...	.15	...	.26	.35	.45 at 60 min.
6	25	Oxygen	.01	...	.15	...	.28	.38	.49 at 60 min.
7	25	Oxygen	.005	.11	.15	.19	.30	.42	.53 at 60 min.
8	25	Oxygen	.003	.10	.15	.20	.30	.42	.55 at 60 min.
9	25	Oxygen	.002	.10	.14	.20	.29	.40	.54 at 60 min.

some slower reaction of the organic material alone controls the speed of the process. The reaction is of the first order with regard to the dixanthyl derivative (Expts. 6, 7, 8, 9, Table I).

Taking into account all that is known concerning the behavior of dixanthyl derivatives, it appears fairly certain that the rate-controlling step is the dissociation of the dixanthyl into free radicals. The mechanism of the oxygen absorption thus appears to be as follows



It is not surprising that the reaction is not subject to those marked catalytic effects which have been noted with so many auto-oxidation processes since it really is not an auto-oxidation which we are measuring. This lack of catalytic influence was clear both from the reproducibility of the results using different samples of dixanthyl compound and bromobenzene and also from the fact that no change was caused by the addition of 0.005% of hydroquinone, 3% of copper-bronze powder, powdered glass or a trace of sodium cyanide. It is further evident why the reaction has a rather unusually high temperature coefficient of the reaction velocity (an increase of 4–5-fold for 10° rise). The dissociation of a carbon–carbon linkage is the sort of process that might be expected to have a high temperature coefficient.

Having established to our own satisfaction the mechanism of the reaction, we then proceeded to a careful study of the rate of the dissociation of the simple alkyl derivatives of dixanthyl. The compounds studied were dimethyldixanthyl, diethyldixanthyl, dipropyldixanthyl, di-*n*-butyldixanthyl, di-n-amyldixanthyl and di-iso-amyldixanthyl. They were prepared and purified by the method described in earlier papers of this series. They were stored in an atmosphere of hydrogen in sealed ampules. Experiments with samples of the same compound prepared and purified at different times showed that the results were reproducible.

Apparatus and Procedure

The reaction vessel consists of a tincture bottle of 50-cc. capacity fitted with a ground-glass stopper carrying an entrance tube which was connected to one side of a manometer by means of about 10 cm. of heavy rubber tubing. Another bottle of the same shape and size was similarly connected with the other side of the manometer. Both bottles fitted into a holder which was immersed in a water thermostat and which was rocked back and forth by a suitable mechanism driven by a small motor. The manometer was of capillary glass tubing and contained bromobenzene colored with methylene blue. The difference in pressure was read on a millimeter scale placed directly beside the capillary tubing. The temperature of the thermostat was constant within ±0.1° and the bottles were completely immersed in the water.

In starting an experiment both bottles were charged with the same volume of bromobenzene (usually 4.0 cc.), oxygen bubbled through for five minutes from a tank, the stoppers quickly inserted and sealed with paraffin. The bottles were then placed in the holder and shaken until the manometer reading was constant; this required from ten minutes to half an hour. This equilibration of the solvent is essential if one wishes to obtain reproducible results with an accuracy of a few per cent. When equilibrium had been established, a sample (about 0.02 *g.)* of dixanthyl derivative was rapidly weighed to a tenth of a milligram in a small bulb with a long neck. This bulb was quickly introduced into the reaction bottle, which was removed from the thermostat and opened for a few seconds for this purpose. The stopper was sealed as before and the bottle placed in the thermostat for five minutes. During this time the sample did not come in contact with the solvent since the neck of the bulb-tube rested against the side of the vessel, keeping the tube upright. The levels of the manometer were now made equal by bringing both sides to atmospheric pressure by means of two three-way cocks. The cocks were then turned so that each side of the manometer was connected directly to one bottle. The bulb tube was now broken by one or two rapid shakes of the reaction bottle, which was immediately replaced in the holder and the shaking device started. The time was taken from this point and the manometer read. To assist in the rapid breaking of the bulb-tube a sharp pointed rod was usually inserted in the bulb-tube before it was placed in the reaction vessel. The solid dixanthyl derivative dissolves very rapidly; the error introduced by the time required for complete solution is probably slight and affects only the first few readings.

From the change in pressure as read on the manometer the volume of oxygen which has been absorbed may be calculated. In order to do this it is necessary to know the volume of gas displaced by the rise of the liquid in the manometer tube. This was found, by weighing a column of mercury, to be 0.006 cc. per centimeter. The total volume above the solution on each side of the system was 62 cc. The fraction of dixanthyl derivative which has reacted at any given time is equal to the volume of oxygen absorbed divided by the amount calculated on the assumptions in regard to the reaction discussed above (one mole of oxygen per mole of substance). The expression for this fraction, Z, in terms of the data just given and the difference in pressure expressed in millimeters of mercury, b, the barometric pressure P, the vapor pressure of C_6H_5Br, β, the weight of sample, w, and the molecular weight of the material (M.W.) is given in Equation 1, which is readily derived by an application of the gas laws.

$$Z = \frac{62b(0.0054P - 0.0054\,\beta + 62) - (0.0027)^2b^3}{(62 + 0.0027b)RT} \times \frac{\text{M. W.}}{w} \tag{1}$$

The term $(0.0027)^2b^3$ in the numerator and $0.0027b$ in the denominator may be neglected since b is never greater than 10. Variations in the barometric pressure between 750 and 770 mm. introduce errors less than the probable error of our measurements; the vapor pressure of bromobenzene may also be neglected. Taking an average value of P as 760, neglecting the terms just mentioned and substituting $m/9.05$ for b, where m is the pressure difference in millimeters of bromobenzene, we have Equation 2.

$$Z = 1.172 \times 10^{-4} m \frac{\text{M. W.}}{wT} \qquad (2)$$

Discussion of Results

A few typical experiments are reported in full in Table II. The same results are shown graphically in Fig. 2, in which $-\log (1-Z)$ (where Z = fraction reacted) has been plotted against the time in minutes. The straight line was drawn to pass through the greatest number of points. The slope of this line multiplied by *2.303* is the value of k, the usual velocity constant of a first-order reaction. Using this value of k, values of Z have been calculated corresponding to the experimental points. The agreement between the values thus calculated and those found is shown in the last columns of Table II. It is evident that the reaction rate corresponds within the experimental error to that of a monomolecular reaction over the range studied. It will be noted that in Fig. *2* the straight lines do not pass through the origin. This is probably because the initial time is uncertain, in part due to the time required for solution of the material. By using this graphical method of obtaining the best value of k, this error has been largely eliminated. The two curves A and B in Pig. *2* and the corresponding data in Table II were chosen as representative of the most satisfactory and the least satisfactory of our duplicate experiments.

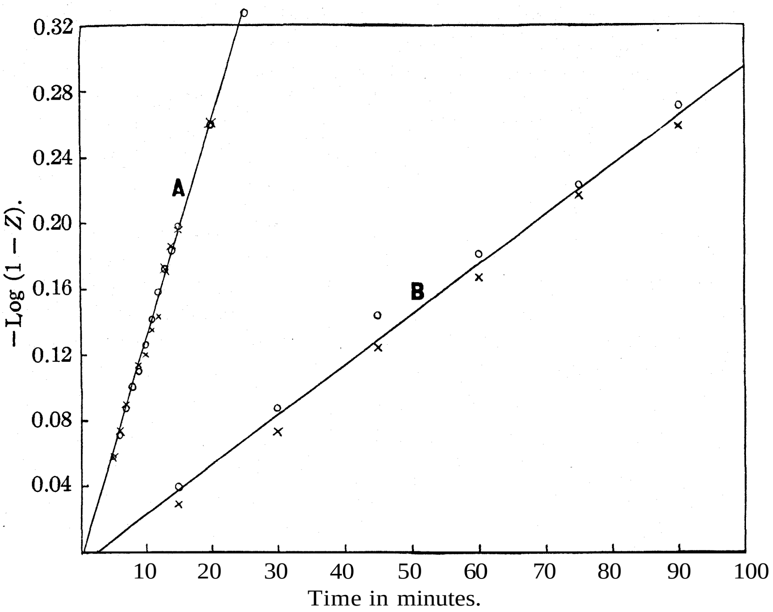


Fig. 2.—The rate of dissociation of dixanthyl derivatives as measured by rate of oxygen absorption: typical results. Curve **A** corresponds to Expt. 1, Table II; Curve B to Expt. 2; the crosses and circles indicate the points in the two duplicate runs.

TABLE II

TYPICAL DATA OBTAINED IN DUPLICATE EXPERIMENTS

(A) Substance = di-n-amyldixanthyl; solvent = bromobenzene; temp. = 35°.

Time, min.	Press., mm. of C_6H_5Br, m	Frac. reacted, Z	Frac. reacted, calcd., $k = 30.6 \times 10^{-3}$	Diff.	Time, min.	Press., mm. of C_6H_5Br, m	Frac. reacted, Z	Frac. reacted, calcd., $k = 30.6 \times 10^{-3}$	Diff.
		Expt. 1					Expt. 2		
5	14	0.124	0.128	−0.004	5	13.5	0.125	0.128	−0.003
6	17	.150	.157	− .007	6	17.0	.157	.157	0
7	20.5	.181	.182	− .001	7	20.5	.189	.182	+ .007
8	23.5	.208	.208	0	9	25.0	.231	.231	0
9	25.5	.225	.231	− .006	10	26.5	.242	.254	− .012
10	28.5	.252	.254	− .002	11	29.0	.268	.277	− .009
11	31.5	.278	.277	+ .001	12	30.5	.281	.298	− .017
12	34.5	.305	.298	+ .007	13	35.5	.327	.320	+ .007
13	37.0	.327	.320	+ .007	14	37.5	.346	.344	+ .004
14	39.0	.344	.344	0	15	39.5	.364	.360	+ .004
15	41.5	.366	.360	+ .006	20	49.0	.452	.444	+ .008
20	51.0	.451	.444	+ .007	25	57.0	.526	.526	0
25	57.5	.508	.526	− .018					

Expt. 1, $Z = 0.008839\, m$ (from Equation 2 by substituting values for w, M. W., T). Expt. 2, $Z = 0.009223$ m.

(B) Substance = di-n-amyldixanthyl; solvent = bromobenzene; temp. = 25°.

Time, min.	Press., mm. of C_6H_5Br, m	Frac. reacted, Z	Frac. reacted, calcd., $k = 6.95 \times 10^{-3}$	Diff.	Time, min.	Press., mm. of C_6H_5Br, m	Frac. reacted, Z	Frac. reacted, calcd., $k = 6.95 \times 10^{-3}$	Diff.
		Expt. 1					Expt. 2		
15	9.5	0.087	0.081	+0.006	15	7.0	0.066	0.081	−0.015
30	20.0	1	.174	+ .009	30	16.5	.155	.174	− .019
45	31.0	.283	.255	+ .028	45	26.5	.249	.255	− .006
60	37.5	.342	.330	+ .012	60	34.0	.320	.330	− .010
75	44.0	.402	.396	+ .006	75	41.9	.394	.396	− .002
90	50.7	.464	.456	+ .008	90	48.0	.450	.456	− .006
105	56.0	.511	.510	+ .001	105	54.0	.507	.510	− .003

Expt. 1, $Z = 0.009135m$; Expt. 2, $Z = 0.009396\, m$.

In Table III are summarized all of our final measurements. The values of k were obtained by the graphical method illustrated by Fig. 2. We consider the value of k for each compound at each temperature to be subject to an error of not more than ±3%.

In Fig. **3** the values of log k are plotted against the reciprocal of the absolute temperature, the slope of each line multiplied by 2.303 being the value of E/R in the equation $d \ln k/dT = -E/RT^2$. The values of E calculated from the integrated form of this equation are given in Table III. The average values for the dimethyldixanthyl (34,000) and diethyldixanthyl (29,000) are higher than the average for all the other compounds (26,000–27,100). This difference appears to be outside the experimental error. It is perhaps significant that the larger value of E corresponds to

TABLE III

SUMMARY OF RESULTS

All measured in bromobenzene; concn. = 0.01 *M*, oxygen employed.

Subs. and its m. p., °C.	Temp., °C.	No of expts	Total no of points	Av. value of k X 103 (graphically)	*E* in cal			
					15–25'	25–35'	25°–40°	Average
Dimethyldixanthyl,	25	2	21	1.79		35,700		
179–180°	35	3	13	12.6			32,200	34,000
	40	2	15	24.3				
Diethyldixanthyl,	25	2	19	1.99		27,700		
191–193°	35	2	14	9.09				29,000
	40	2	17	2 3 1			30,400	
Di-n-propyldixan-	25	3	16	11.9		26,700		26,700
thyl, 179–180°	35	2	16	51.4				
Di-n-butyldixanthyl,	15	4	34	2.48	29,700			
162–163°	25	2	18	1 2 6		25,200		
	30	2	13	26 3			24,400	
	35	2	8	50.0				
	40	2	12	90 4				26,000[a]
Di-*iso*-amyldixan-	25	2	12	9.99				
thyl, 161°						26,200		26,200
	35	2	10	42.0				
Di-*n*-amyldixanthyl,	25	2	16	6.95				
94–96°						27,100		27,100
	35	2	25	30.6				

[a] Values for 15 to 30° (27,300) and for 30 to 40° (23,300) included in this average.

a lower value of k at a given temperature, though the ratio E/T_x (where T_x = the temperature at which $k \times 10^3 = 10$) varies from 110 for the methyl compound to 87.5 for the n-butyl compound. It seems unlikely that all this variation in E/T_x is due to experimental errors.

It is evident from Table III and Fig. 3 that the methyl and ethyl compounds cannot be distinguished the one from the other by our measurements. On passing from the ethyl to the n-propyl compounds there is an increase in k of six-fold, the normal propyl and butyl compounds are practically identical in their rates, but the n-amyl compound is somewhat slower. On the other hand, the iso-amyl compound is almost as rapidly dissociated as the n-propyl and n-butyl. The relationship between these higher homologs at 25° is n-C_5H_{11}:*iso*-C_5H_{11}:C_3H_7:C_4H_9 as 1:1.4:1.7:1.8. The practical identity in behavior of the methyl and ethyl compounds is somewhat surprising. In connection with the problem of the relationship between structure and speed of dissociation (the k of Table III), it must be remembered that di-isobutyldixanthyl (R = $(CH_3)_2CHCH_2$-) and dibenzyldixanthyl (R = $C_6H_5CH_2$-) absorb oxygen too rapidly for accurate measurements at room temperature (values of $k \times 10^3$ estimated as > 300) and the di-*iso*propyldixanthyl is appreciably dissociated in solution at room temperature and behaves like hexaphenylethane.

The parallelism between the rate of dissociation and the temperature required for appreciable dissociation (as judged by the color) in a 0.05 M solution is shown in Table IV. We have also included in this table some tests made by Dr. A. W. Sloan in this Laboratory on the rate of the reaction between a chloroform solution of the dixanthyl derivative and a dilute aqueous solution of ferric chloride and potassium ferricyanide. This reaction results in the more or less rapid formation of Prussian blue, presumably by virtue of the oxidation of the dixanthyl derivative to the corresponding carbinol and the reduction of the iron compound. If this reaction proceeds through the free radical (as it certainly does in certain cases),[3] the rate of the process might, like the rate of oxygen absorption, be controlled by the rate of dissociation. The results given in Table IV indicate that this is probably the case.

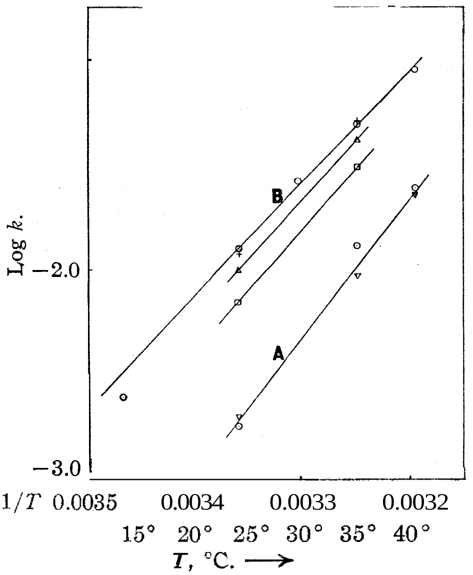


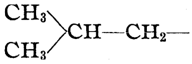
Fig. 3.—The rate of dissociation of dixanthyl derivatives at different temperatures. Line A, ○, dimethyldixanthyl; ▽, diethyldixanthyl. Line B and two shorter lines, ○, di-*n*-butyldixanthyl; +, di-*n*-propyldixanthyl; A, di-*iso*-amyldixanthyl-; □, di-*n*-amyldixanthyl.

It is clear from an inspection of Table IV that the measurements of the rate of oxygen absorption, the Prussian blue test and the appearance of color on heating, all place the compounds in the same groups and that the differences in each case are of the same order of magnitude. If ΔH for the dissociation is approximately the same for all dixanthyl derivatives, the figures in Col. 4 of Table IV may be taken as an indication of the order of the relative values of log K at 25° since $d \ln K/d(1/T) = \Delta H/R$. The higher temperature corresponds to the larger value of $-\log$ K. Since the dissociation constant $K = k_{\text{diss}}/k_{\text{ass.}}$, it is interesting that from Table IV there appears to be at least a rough parallelism between $k_{\text{diss.}}$ (the rate of dissociation) and the equilibrium constant, K. This suggests the possibility that the speed of association of the free radicals (in solution) is practically the same for all these related compounds. This might well be the case if the rate of association of these very reactive molecules were limited only by the number of collisions; this number would be essentially independent of the chemical nature of the free radicals themselves.

[3] Conant, THIS JOURNAL, 47, 1959 (1925).

Table IV

Comparison of the Rate of Dissociation of Dixanthyl Derivatives and the Temperature Required for Appreciable Dissociation

Subs. groups	Approx. rate of diss. in C_6H_5Br at 25°, $k \times 10^3$	Time req. for Prussian Blue Test (see below), min.[a]	Temp.[b] at which "appreciable color" dev. in a 0.05 M soln. in $C_6H_5COOC_2H_5$
CH_3	2	35	210°
C_2H_5		..	
n-C_4H_9	10	20	160°
n-C_3H_7		..	
iso-C_5H_{11}		15	
$C_6H_5CH_2$—	Estimated >300	0.2	100°
 $(CH_3)_2CH—CH_2—$		..	

[a] The Prussian blue test was carried out as follows: a few milligrams of the substance was dissolved in 3 cc. of chloroform and placed in a test-tube with 5 cc. of a very dilute aqueous solution of ferric chloride and potassium ferricyanide. The mixture was shaken vigorously for one minute and then allowed to stand. In the case of the most reactive dixanthyl derivatives there was an almost immediate formation of a blue precipitate; with the less reactive compounds the precipitate slowly formed at the interface between the solvents.

[b] The temperatures recorded in the fourth column were estimated by rapidly heating 0.05 M solutions (in $C_6H_5COOC_2H_5$) sealed in an inert atmosphere to 100, 160, 190, 210" and estimating the color by comparison with standards of dilute potassium dichromate solution. We estimate that the yellow color taken as "appreciable color" corresponds to about 1% dissociation but this value is, of course, very uncertain. Since all the experiments were performed exactly alike we feel that the relative temperatures required for the same degree of dissociation are significant and are probably correct within ±5°. The color due to dissociation was, of course, lost on cooling. Further information in regard to the reversible thermal coloring of the solutions has been given in the earlier papers of this series.

We hope to obtain further information along this line as a result of the studies which are now in progress in this Laboratory on the energetics and kinetics of free radical formation.

Summary

1. The rate of oxygen absorption of di-n-butyldixanthyl in bromobenzene solution at 25° has been measured by means of a differential pressure apparatus. The reaction is of the first order until about half a mole of oxygen per mole of dixanthyl derivative has been absorbed. The rate is independent of the concentration of the oxygen in the solution. It thus appears that the rate-controlling step is the dissociation of the dixanthyl derivative into a free radical.

2. The rates of dissociation of the following dixanthyl derivatives in bromobenzene have been measured at different temperatures by following the rate of oxygen absorption: dimethyl, diethyl, di-n-propyl, di-*n*-butyl,

di-n-amyl, di-iso-amyl. The energy of activation has been calculated from the temperature coefficient of the reaction velocity.

3. A parallelism has been found between the rates of dissociation and the temperature at which appreciable dissociation first occurs as evidenced by the appearance of color in a dilute solution.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

PHENANTHRENEQUINONES RELATED TO ALIZARIN AND PURPURIN

BY LOUIS FREDERICK FIESER

RECEIVED MARCH 2, 1929 PUBLISHED JUNE 5, 1929

It is an interesting indication of the general difference in the chemistry of anthracene and of phenanthrene that alizarin was synthesized, produced commercially and the structure established all in the course of seven years, while over fifty years have elapsed since the first attempt was made[1] to obtain the corresponding phenanthrene derivative and the substance has not yet been described. Phenanthrenequinone is so sensitive to the action of alkalies, acids and oxidizing agents that it is doubtful if many of its derivatives will prove useful as dyestuffs; but the angular alignment possesses a greater chromophoric character than anthraquinone, and it is at least a matter of theoretical interest to know how the phenanthrenequinones having two or more hydroxyl groups in the ortho and para positions compare with the anthraquinone dyes.

Morpholquinone, the first substance of this type to be described, was obtained by Vongerichten[2] from a degradation product of morphine. Because it was a mordant dye similar to alizarin, Vongerichten at first regarded it as 1,2-dihydroxyphenanthrenequinone, but later[3] recognized it as the 3,4-isomer. The aim of several investigators to prepare this quinone from phenanthrene, or by applying the Pschorr synthesis, was finally achieved by Schmidt and Söll.[4] An unsuccessful attempt to synthesize 1,2-dimethoxyphenanthrene, from which 1,2-dihydroxyphenanthrenequinone might be obtainable, has been recorded,[5] and Mukherjee and Watson[6] found it impossible to hydroxylate 2-hydroxyphenanthrenequinone by the methods so useful for the preparation of alizarin and its congeners. Thus no dihydroxyphenanthrenequinones possessing dyeing properties, other than morpholquinone, were known until Brass under-

---

[1] Graebe, *Ann.*, 167, 143 (1873).

[2] Vongerichten, *Ber.*, 32, 1521 (1899).

[3] Vongerichten, *ibid.*, 33, 352 (1900).

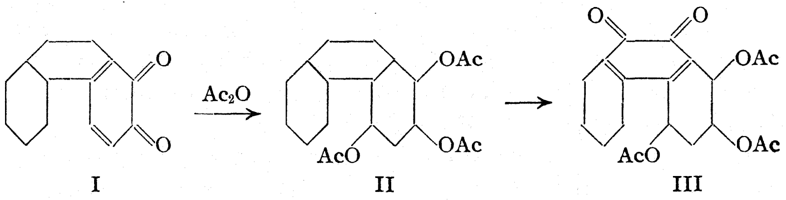
[4] Schmidt and Söll, *ibid.*, 41, 3696 (1908).

[5] Pschorr and Buckow, *ibid.*, 33, 1829 (1900).

[6] Mukherjee and Watson, J. Chem. *Soc.*, 109, 617 (1916).

took a study of the rearrangement of the phenanthrenequinone azides. As a result of this work he was able to prepare 1,4-dihydroxyphenanthrenequinone[7] and the 2,3-isomer.[8] The only other polyhydroxyphenanthrenequinones known are 2,5-[9] and 2,7-dihydroxyphenanthrenequinone,[10] 2,3,4-trihydroxy-[11] and 2,7,?-trihydroxyphenanthrenequinone,[6] and 2,3,6,7-tetrahydroxyphenanthrenequinone.[12] None of these compounds presents any new points of interest.

In view of the scarcity of such compounds and the difficulty in finding methods suitable for their preparation, it seemed worth while to attempt to use the isophenanthrenequinones which recently have become available for the preparation of new 9,10-phenanthrenequinones. Thus an improved method of preparing morpholquinone has been found in the reductive acetylation of 3,4-phenanthrenequinone, followed by oxidation at the 9,10-positions and hydrolysis of the oxidation product.[13] In a similar manner 1,2-phenanthrenequinone[14] has now been converted into 1,2-dihydroxyphenanthrenequinone. The triacetate of 1,2,4-trihydroxyphenanthrenequinone, III, was obtained by hydroxylating 1,2-phenanthrenequinone, I, by the Thiele method and oxidizing the triacetoxy-phenanthrene, II, with chromic acid. 1,3,4-Trihydroxyphenanthrenequinone was prepared in the same way from 3,4-phenanthrenequinone.



The oxidation of an acetoxyl or alkoxyl derivative of phenanthrene seldom proceeds smoothly and in good yield, and the results are often negative. Thus Pschorr reports the failure to obtain a quinone from 1- or 4-methoxyphenanthrene, or from 1,5-dimethoxy-6-acetoxyphenanthrene,[15] and the author was unable to oxidize 3-methoxy-1,4-diacetoxyphenanthrene or 1-(*p*-toluidino)-3,4-diacetoxyphenanthrene.[13] The difficulty is partly due to the fact that the quinones are about as easily oxidized as the starting materials,[3] while a poor yield in some cases has been traced

[7] Brass and Stadler, Ber., **57,** 134 (1924).

[8] Brass, Ferber and Stadler, *ibid.*, 57, 121 (1924).

[9] Schmidt and Kämpf, *ibid.*, 36,3750 (1903).

[10] Anschiitz and Meyer, *ibid.*, 18, 1944 (1885).

[11] Schmidt and Spoun, Ber., 55,1194 (1922).

[12] Brass and Nickel, *ibid.*, 58, 204 (1925).

[13] Fieser, THIS JOURNAL, 51,940 (1929).

[14] Fieser, *ibid.*, 51, 1896 (1929).

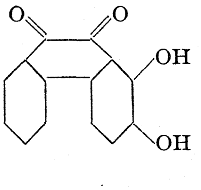
[15] Pschorr, Rer., 33,161, 176, 1826 (1900).

to the formation of a diphenanthryl derivative as a by-product.[16] In the present case the chief side reaction appeared to consist in the hydrolysis of the acetoxyquinones or of the starting materials, but, by carrying out the oxidation with an equal weight of chromic acid in glacial acetic acid solution at 40°, yields of from **30** to 60% were obtained.

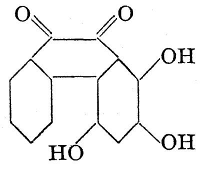
The new trihydroxyphenanthrenequinones are very easily oxidized by the air in alkaline solution. The intensely green solutions lose their color in a short time and it is thus necessary to hydrolyze the acetates in an indifferent atmosphere. 1,2-Dihydroxyphenanthrenequinone and morpholquinone are also oxidized under these conditions, though not as rapidly. Since this sensitivity to oxygen is characteristic only of the quinones having hydroxyl groups in the ortho or para positions, it is probable that the first step in the oxidation is the formation of a diquinone.

It may be noted that the new quinones exhibit no tendency to exist in any of the possible tautomeric forms, for they are all reconvertible into the original acetates, whose structures are fixed.

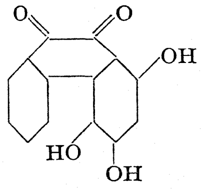
The new hydroxyphenanthrenequinones are in general inferior in dyeing properties to the isomers of the anthraquinone series. The trihydroxy-*o*-quinones, V and VI, are very poor dyes in comparison with purpurin. 1,2-Dihydroxyphenanthrenequinone, IV, which corresponds in structure to alizarin, dyes mordanted wool deep green, but it has little affinity for unmordanted cloth. The colors produced with IV are, to be sure, deeper than those from alizarin, just as 1,4-dihydroxyphenanthrenequinone surpasses quinizarin in tinctorial properties.[17] This is a further indication that phenanthrenequinone is a more powerful chromophore than anthraquinone.



IV



V



VI

On comparing the descriptions of the dyeing produced with the three o-dihydroxyphenanthrenequinones, it is found that there is a deepening in color on passing from the 2,3-isomer (brown-red),[8] to the 3,4-isomer (blue),[2] to the 1,2-isomer (green). It is rather surprising that the isomer having the true "alizarin structure" has less affinity for the fiber and gives less brilliant colors than morpholquinone. An hydroxyl group adjacent to the carbonyl group of phenanthrenequinone does not appear to favor

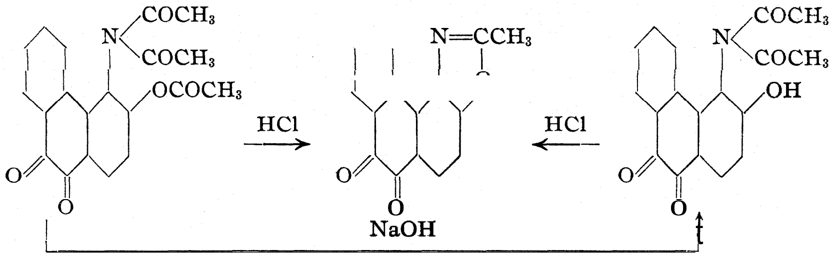
---

[16] (a) Vongerichten, Ber., 30, 2441 (1898); (b) Werner, Ann., 322, 135 (1902).

[17] Brass, *Z. angew. Chem.*, 37, 67 (1924).

particularly the formation of a color lake.[18] Dimroth and Roos recently have recorded a similar observation concerning the dihydroxynaphthoquinones.[19] It is also surprising that the trihydroxyphenanthrenequinones, V and VI, are much poorer dyes than the ortho or para dihydroxy compounds from which they may be considered to be derived.

Since Brass[7,8] has found that 2-amino-3-hydroxy- and 4-amino-1-hydroxyphenanthrenequinone possess some dyeing properties, an attempt was made to prepare the quinone corresponding to 4-amino-3-hydroxyphenanthrene.[13] The triacetate of this substance was converted without difficulty into the triacetate of 4-amino-3-hydroxyphenanthrenequinone, VII, but the complete hydrolysis of the latter compound was not accomplished. On acid hydrolysis, or by dissolution of the quinone in bisulfite solution, the substance was converted into the oxazole derivative, VIII, which is very resistant to the action of either acids or alkalies. The triacetate was easily hydrolyzed by alkalies, but the product obtained was the N,N-diacetate, IX. This compound was easily converted into the oxazole derivative, VIII, by the action of acids, but it was only very slowly attacked by alkalies and then only with the complete destruction of the molecule. Thus the desired aminohydroxyphenanthrenequinone was not obtained.



VII VIII IX

The stability of the diacetylamino group in the 4-position is somewhat surprising, but it is not unlike the unusual stability of the sulfonic acid group of 1,2-phenanthrenequinone-4-sulfonic acid.[14] In the latter case the phenomenon was attributed to the configuration of the molecule, and it is possible that the resistance of the above diacetate to alkaline hydrolysis is due to the blocking effect of the neighboring phenyl group.

Experimental Part

1,2-Diacetoxyphenanthrene.—A mixture of equal parts of 1,2-phenanthrenequinone,[14] zinc dust and sodium acetate, with 5 parts of acetic anhydride, was boiled until the solution became pale yellow, the mixture was diluted with glacial acetic acid,

---

[18] 1-Hydroxyphenanthrenequinone, which will be described in a forthcoming paper, imparts only a faintly pink color to mordanted wool.

[19] Dimroth and Roos, *Ann.*, 456,177 (1927).

filtered and carefully treated with water. The crude diacetate, m. p. 140°, was thus obtained in 89% yield. After repeated crystallization from dilute acetic acid and from ligroin-benzene, small, colorless needles melting at 146–147° were obtained. The compound is very readily soluble in benzene or glacial acetic acid and sparingly soluble in ligroin.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.45; H, 4.79. Found: C, 73.24; H, 4.82.

1,2-Diacetoxyphenanthrenequinone.—Five grams of the diacetate was oxidized in glacial acetic acid solution at 40° with 5.2 g. of chromic acid. The mother liquor contained some unchanged diacetate, for a further quantity of the quinone was obtained by adding more chromic acid after collecting the first crop of crystals. The yield was 3.3 g. (60%). The quinone dissolves readily in glacial acetic acid and forms small orange needles which melt with decomposition at 251° (257°, corr.).

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.65; H, 3.73. Found: C, 66.89; H, 3.85.

1,2-Dihydroxyphenanthrenequinone.—When the diacetate was covered with a mixture of sodium hydroxide and alcohol, hydrolysis took place at once. A dark green solution resulted and some of the sodium salt of the quinone separated. The mixture was diluted with water in order to bring the salt into solution, and acidified. The flocculent, dark red precipitate was digested for a short time at the boiling point and the more compact product was then easily collected and washed. The substance is only sparingly soluble in water, and very readily soluble in alcohol, acetone or glacial acetic acid. Clusters of small, very dark red crystals were obtained from acetone. The substance decomposes on heating. The alkaline solution is chrome green, and a green salt is easily precipitated by an excess of alkali. The solution in concentrated sulfuric acid is red; in pyridine it is crimson.

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.77; H, 3.48.

1,2-Dihydroxyphenanthrenequinone dyes unmordanted wool a pale bluish gray. Wool or silk mordanted with aluminum or chromium is dyed dark green. The tones are not as brilliant as those with morpholquinone.

1,2,4-Triacetoxyphenanthrenequinone.—In early experiments on the oxidation of 1,2,4-triacetoxyphenanthrene[14] it was found that the product was partially hydrolyzed when the reaction was carried out in glacial acetic acid solution at the boiling point, with the result that most of it was destroyed by further oxidation. The use of acetic anhydride, or of mixtures of this with acetic acid, was then tried but a somewhat elevated temperature was required and again hydrolysis products of the quinone, as well as of the starting material, were obtained. Thus 2-acetoxy-1,4-phenanthrenequinone (m. p. 146°) was identified in one experiment. More satisfactory results were obtained by dissolving 5 g. of the triacetate in 75 cc. of glacial acetic acid, cooling to 40° and adding a solution of 5 g. of chromic acid. The product, which separated after standing for some time, was washed with alcohol and crystallized from toluene, giving 1.7 g. (32%) of pure material. It forms orange plates melting with decomposition at 227–228°. The quinone is only moderately soluble in toluene and readily soluble in glacial acetic acid.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.63; H, 3.72.

1,2,4-Trihydroxyphenanthrenequinone.—While the triacetate is very easily hydrolyzed, the extreme sensitivity of the hydroxyquinone to oxygen in the presence of alkali makes it imperative to exclude all air while carrying out the reaction. When the triacetate was covered with alcoholic sodium hydroxide solution in an atmosphere of nitrogen, hydrolysis proceeded without heating, giving a deep green solution. The green solution was diluted with water, filtered and acidified. The precipitate was at first somewhat gelatinous, but it coagulated on heating to give an easily filterable suspension. The dried material is black and decomposes on heating. No satisfactory method of crystallizing the compound was discovered. It is sparingly soluble in most solvents other than alcohol, in which it is extremely soluble. The red alcoholic solution deposited a red crystalline crust on slow evaporation, but this product, dried in vacuum at 100°, appeared to contain alcohol of crystallization.

Anal. Calcd. for $C_{14}H_8O_5 \cdot C_2H_5OH$: C, **66.24**; H, **4.32.** Found: C, **66.18**; H, **4.31.**

The precipitated material gave the following analytical results.

Anal. Calcd. for $C_{14}H_8O_5$: C, **65.62**; H, **3.15.** Found: C, **65.30**; H, **3.20.**

This quinone gives a green solution in alkali, but in the presence of air the color rapidly disappears and gives place to a pale red. The change may be noted in the film formed on shaking the green solution in a test-tube. A completely oxidized solution gives off carbon dioxide on acidification. The quinone dissolves in concentrated sulfuric acid with a green color. The solution in pyridine is cornflower-blue when fresh, but soon becomes brown on exposure to the air and deposits a black, sparingly soluble substance which has the properties of a quinone. The trihydroxyquinone is easily acetylated with acetic anhydride and sulfuric acid without heating, giving the original triacetate.

1,2,4-Trihydroxyphenanthrenequinone has scarcely any dyeing properties. A poor, dull brown is produced on aluminum-mordanted wool.

1,3,4-Triacetoxyphenanthrene.—This compound was obtained in good yield by the reductive acetylation of 3-hydroxy-1,4-phenanthrenequinone[13] with zinc dust, sodium acetate and acetic anhydride. It dissolves very readily in alcohol, readily in benzene and only sparingly in ligroin. Fluffy clusters of silken white needles melting at 138° were obtained on crystallization from benzene–ligroin.

Anal. Calcd. for $C_{20}H_{16}O_6$: C, **68.16**; H, **4.58.** Found C, **68.19**; H, **4.67.**

1,3,4-Triacetoxyphenanthrenequinone.—The above triacetate was oxidized in glacial acetic acid solution at 40° with an equal weight of chromic acid. After maintaining the specified temperature until yellow crystals of the quinone began to separate, the mixture was cooled and the nearly pure product was collected; yield, **47%.** The compound dissolves readily in glacial acetic acid and crystallizes from this solvent in the form of well-shaped yellow needles. The substance softens at about 220° and decomposes at about **240°**.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, **62.82**; H, **3.69.** Found: C, **62.66**; H, **3.92.**

1,3,4-Trihydroxyphenanthrenequinone.—Working in an atmosphere of nitrogen, 1,3,4-triacetoxyphenanthrenequinone was covered with cold alcoholic sodium hydroxide solution. Hydrolysis took place readily and the solution became deep red and then green. A dark red, rather voluminous precipitate was thrown down on acidification. The product is only sparingly soluble in water but very readily soluble in alcohol, and it was obtained in the form of small, very dark red crystals on allowing the intensely red alcoholic solution to evaporate slowly.

Anal. Calcd. for $C_{14}H_8O_5$: C, **65.62**; H, **3.15.** Found: C, **65.47**; H, **3.25.**

The solution in alkali is intensely green when viewed in thin layers, but greenish-red when a considerable volume of the solution is viewed against a source of light. When exposed to the air, the color of the alkaline solution fades rather rapidly to a pale pink. The solution in concentrated sulfuric acid is deep red, while with pyridine a deep red solution is obtained which becomes green on dilution with water. The substance is easily acetylated by acetic anhydride, either in pyridine solution or with the aid of a few drops of concentrated sulfuric acid.

1,3,4-Trihydroxyphenanthrenequinone has poor dyeing properties. It dyes aluminum-mordanted wool or silk a dull green; with a chromium mordant a brown-gray is produced.

4-Amino-3-phenanthrol **Diacetate.**—This substance was prepared by adding acetic anhydride to a cold solution of 4-amino-3-phenanthrol hydrochloride[13] in pyridine. The product was precipitated by water and crystallized repeatedly from alcohol. It formed small, colorless plates melting at 208° (211°, corr.). It is sparingly soluble in benzene, moderately soluble in alcohol and insoluble in acids or alkalies.

Anal. Calcd. for $C_{18}H_{15}O_3N$: C, 73.69; H, 5 16. Found: C, 73.38; H, 5.11.

Oxazole Derivative of 4-Amino-3-phenanthrol.—Aminophenanthrol diacetate readily loses the elements of acetic acid on heating, with the closing of an oxazole ring. Since the same substance is formed by the loss of acetic anhydride from the triacetate,[20] a mixture of the di- and triacetates may be used for the preparation.

A mixture of 24.5 g. of 4-amino-3-phenanthrol hydrochloride, 9 g. of fused sodium acetate and 50 cc. of acetic anhydride was heated for one hour on the water-bath and the product was poured into water. The rather oily solid was heated in a distilling flask until all of the adhering water and all of the acetic acid formed in the reaction had been removed. The residue was then distilled at a pressure of 3 mm. The distillate solidified at once, giving 20 g. (86%) of a pale yellow product melting at 152°. Repeated crystallization from glacial acetic acid failed to remove the color, but yielded small, pale yellow plates melting at 155°.

Anal. Calcd. for $C_{16}H_{11}ON$: C, 82.37; H, 4.76. Found: C, 82.23; H, 5.02.

The substance dissolves readily in glacial acetic acid or benzene; it is moderately soluble in alcohol and insoluble in acids or alkalies.

Oxazole Derivative of 4-Amino-3-hydroxyphenanthrenequinone.—A solution of 4.7 g. of the above phenanthrene derivative in 150 cc. of glacial acetic acid was cooled to 70° and a solution of 8 g. of chromic acid (twice the theoretical quantity) in water, diluted with glacial acetic acid, was added in the course of ten minutes, while maintaining the initial temperature by cooling. In the early stages of the oxidation a brown precipitate was produced but this soon dissolved and orange crystals began to separate. After cooling the solution the product was collected and washed with alcohol. It was nearly pure; yield, 2.4 g (47%).

Crystallized from glacial acetic acid, in which it is only moderately soluble, this quinone formed small, orange needles melting at 275° (282°, corr.). It dissolves in concentrated sulfuric acid with a red-brown color and may be recovered unchanged from the solution. It dissolves to a slight extent in hot concentrated bisulfite solution and is recovered on the addition of acid or alkali to the solution. Attempts to hydrolyze this oxazole derivative with alcoholic sodium hydroxide solution were unsuccessful. The substance was attacked with such difficulty that the primary products were apparently destroyed during the process.

Anal. Calcd. for $C_{16}H_9O_3N$: C, 72.99; H, 3.45. Found: C, 72.78; H, 3.71.

4-Amino-3-hydroxyphenanthrenequinone Triacetate.—Werner[20] obtained triacetylaminophenanthrol by heating the aminophenanthrol with acetic anhydride in a sealed tube. It may be prepared more easily by boiling a mixture of 12 g. of 4-amino-3-phenanthrol hydrochloride, 4 g. of fused sodium acetate and 90 cc. of acetic anhydride for one hour. The mixture was poured into water and the product crystallized from alcohol; yield, 12.5 g. (76%); m. p., 170.5" (Werner, 169–170").

The conversion of the triacetate into a quinone was best accomplished by oxidizing a solution of 4 g. of material in 30 cc. of glacial acetic acid with a solution of 4 g. of chro-

---

[20] Werner, *Ann.*, 321, 298 (1902).

mic acid in 4 cc. of water and 8 cc. of glacial acetic acid at 55-60'. After ten minutes a little water was added gradually to the red solution; the quinone then separated in crystalline condition and was practically pure. The compound slowly dissolves on boiling with a rather large quantity of alcohol, but the resulting solution deposits crystals only after it has been concentrated to about one-tenth of the initial volume. Feather-shaped clusters of yellow needles melting at 204° (207°, corr.), with decomposition, are thus obtained.

Anal. Calcd. for $C_{20}H_{15}O_6N$: C, 65.74; H, 4.14. Found: C, 65.84; H, 4.45.

The only compounds isolated as the result of the hydrolysis of this substance were the oxazole derivative and a diacetate. The former is produced by boiling the alcoholic solution with hydrochloric acid, or by dissolving the quinone in bisulfite solution and adding hydrochloric acid.

4-Diacetylamino-3-hydroxyphenanthrmequinon—his was obtained by the alkaline hydrolysis of the triacetate. Working in an atmosphere of nitrogen, 2 g. of the triacetate was covered with 5 cc. of alcohol and 8 cc. of *3N* sodium hydroxide solution. The material rapidly dissolved to give a clear, deep red solution. When the solution was diluted with water and then acidified, a yellow solution resulted and in a short time yellow needles began to separate. The product (1.4 g.) did not dissolve easily in 95% alcohol, but the addition of a little water to a suspension which had been boiled for some time caused the material to go into solution rapidly. Crystallization now took place only after the solution had been well concentrated. Brown-yellow needles of what appeared to be the N,N-diacetate were thus obtained. The compound decomposes on heating at about 255–260°.

Anal. Calcd. for $C_{18}H_{13}O_5N$: C, 66.86; H, 4.05. Found: C, 66.81, 66.85; H, 4.64, 4.52.

The substance dissolves in alkali with a pure, intensely red color. The compound is slowly oxidized in alkaline solution by the air. It is not at all easily hydrolyzed. A strongly alkaline solution, heated on the water-bath in an atmosphere of nitrogen in order to prevent oxidation, still contained unchanged material after two hours. Hydrolysis products could not be isolated in pure condition. It is probable that further changes occur as rapidly as the hydrolysis. Acid hydrolysis of the diacetate yielded only the oxazole derivative. This reaction is easily brought about by boiling an alcoholic solution or suspension of the diacetate with hydrochloric acid. Orange needles of the oxazole soon separate.

Summary

A description is given of the preparation of 1,2-dihydroxyphenanthrenequinone and of 1,2,4- and 1,3,4-trihydroxyphenanthrenequinone from certain isophenanthrenequinones. An attempt to prepare 4-amino-3-hydroxyphenanthrenequinone met with failure owing to the resistance to hydrolysis of a diacetylamino group in the 4-position.

BRYN MAWR, PENNSYLVANIA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY,
PULP AND PAPER RESEARCH INSTITUTE, McGILL UNIVERSITY]

MECHANISM OF ORGANIC REACTIONS. II. THE "NON-EXISTENCE" OF A MIGRATORY METHYL GROUP IN THE CONVERSION OF GLYCEROL-DI-CHLOROHYDRIN INTO GLYCEROL MONOMETHYL ETHER

BY HAROLD HIBBERT AND MYRON S. WHELEN[1]

RECEIVED MARCH 25, 1929 PUBLISHED JUNE 5, 1929

The structure of carbohydrates and polysaccharides rests primarily on the data obtained by preliminary methylation of the material in question, followed by hydrolysis and identification of the resulting methylated product. The assumption has been made throughout that methylation processes are unaccompanied by (a) ring scission or ring shift, or (b) migration of one or more methyl groups during the methylation process.[2]

It has long been recognized that certain groups are particularly prone to migrate as, for example, in the case of acyl groups from oxygen to nitrogen[3] and more recently in connection with the wandering of this same type of group in the synthesis or analysis of glycerol esters.[4]

On the other hand, there are only one or two isolated cases known which appear to indicate the possibility of the migration of a methyl group, the most striking of which is that indicated in the conversion of glycerol-α,α'-di-chlorohydrin into the a-monomethyl ether of glycerol, as reported by Gilchrist and Purves.[5] These authors found that glycerol-α,α'-di-chlorohydrin (prepared by the action of hydrochloric acid on epichlorohydrin)[6] on methylation and subsequent hydrolysis yielded glycerol-α-monomethyl-ether and not the β-isomer as was to be expected. In other words, either a wandering of a methyl group had occurred, or the α,α'-di-chlorohydrin used was impure. No experimental details are given as to the actual method of isolating the glycerol-α,α'-di-chlorohydrin used by them.

They suggested the possibility of an impure starting material, although the homogeneous character and identity of the glycerol-α,α'-di-chloro-

---

[1] Holder of Canadian National Research Council Studentship. The authors wish to express their appreciation to the Research Council for their valuable aid and to the Canadian Pulp and Paper Association for further financial support.

Presented by Mr. M. S. Whelen to the Faculty of Graduate Studies, McGill University, Montreal, in May, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Haworth, "Constitution of Sugars," London, **1929**, p. 55.

[3] Raiford and co-workers, THIS JOURNAL, 46,430,2246,2305 (1924).

[4] For a review see Part I of this series, *ibid.*, **51**, 1601 (1929); Fairbourne and Cowdrey (Ref. 12).

[5] Gilchrist and Purves, *J. Chem. Soc.*, *127*, 2738 (1925). For a review of such migrations compare J. *Chem. Soc.*, 129 (1929).

[6] Smith, Z. *physik. Chem.*, **92**, 717 (1918).

hydrin thus prepared had been emphasized by Smith.[6] Furthermore, the experiments of Conant and Quayle,[7] who prepared the *p*-nitrobenzoate from Smith's product in excellent yield, appeared to disprove this idea, since this was found to have properties markedly different from those of the isomeric derivative prepared from glycerol-a,a^1-di-chlorohydrin. In view of this, the evidence offered by Gilchrist and Purves[5] appeared to be so unsatisfactory that considering the importance of the subject it seemed highly desirable to repeat their work taking the greatest possible precautions to utilize materials only after their identity had been definitely established.

It has been found that when pure glycerol-α,a$'$-di-chlorohydrin is methylated, then converted into the acetate, and the latter hydrolyzed, the expected glycerol-&methyl ether is obtained, there being no evidence whatever of any abnormality in the reaction implying a migration of the methyl group.

The glycerol-α,α'-di-chlorohydrin employed boiled constantly at 174 175° and on methylation with silver oxide and methyl iodide yielded a dichloroglycerolmethyl ether from which the unchanged glycerol-di-chlorohydrin was readily removed by washing with hot water. This α,α'-dichloroglycerol-&methyl ether boiled constantly at 156–159° and so far as could be judged from its physical properties represented a homogeneous chemical substance.

This material on heating with an aqueous alcoholic solution of potassium acetate under pressure was converted into the corresponding acetate. The latter on hydrolysis with a 3% aqueous alcoholic solution of hydrochloric acid[8] yielded a glycerol-monomethyl ether (b. p. 123–125° (13 mm.); $d_4^{17} = 1.1321$); yield, **33%.** The identity of this was established not only by its sharp boiling point and density on the one hand[g] but also by its conversion into *p*-nitrobenzylidene-glycerol-β-methyl ether and into the corresponding di-phenyl carbamate on the other.[9]

This synthesis has been repeated several times using glycerol-α,α'-di-chlorohydrin from various sources[10] and it was found that in all other cases the material used was an impure product consisting of a mixture of the isomeric glycerol-α,α'- and α,β-di-chlorohydrins.

It has been shown by Fairbourne and Foster[11] and more recently by Fairbourne and Cowdrey[12] that the structures assigned to many β-substituted monoglycerides are of doubtful value. The latter investigators have prepared a number of "α,β-" disubstituted glycerols from the corre-

---

[7] Conant and Quayle, THIS JOURNAL, 45,2771 (1923).

[8] Gilchrist and Purves used alkali as the saponifying agent.

[9] Hibbert, Whelen and Carter, THIS JOURNAL, 51,302 (1929).

[10] European supply houses.

[11] Fairbourne and Foster, J. Chem. *Soc.*, 128, 3148 (1926).

[12] Fairbourne and Cowdrey, *ibid.*, 129 (1929).

sponding chlorohydrins and found them to be identical with their supposedly "α,α'-" isomerides. It is thus evident that conclusions drawn from results obtained by employing chlorohydrins for such syntheses must be regarded with grave suspicions in so far as they relate to questions of structure. Moreover, it is to be observed from the results of these investigators that migration often takes place when the hydroxyl group of the di-chlorohydrin is esterified by conversion into an acyl group followed by subsequent substitution of the halogen.

In the present investigation it is shown that a primary replacement of the hydrogen in the hydroxyl group of the glycerol di-chlorohydrin by an alkyl radical does not involve any migration during the subsequent hydrolysis and thus indicates that acyl groups are directly concerned, An earlier hypothesis put forward by Gabriel and Ohle[13] suggested that many of these conversions may be due to the formation of propylene oxide through loss of hydrogen chloride either during the reaction, or previously, with the production of an impure starting material, but as pointed out by Fairbourne and Cowdrey,[12] this in any event is evidently only applicable to specific cases.

In the writers' opinion the question of migration is intimately associated with the presence in the β-position of an acyl radical containing a reactive carbonyl group.

Under these conditions, as first pointed out by Fischer,[14] there exists the possibility of the ready formation of an unstable, intermediate, cyclic ester (Fischer's ortho-ester), which in undergoing spontaneous decomposition permits of a transfer of the acyl group in question.

The four cases reported in the literature involving a migration from the a- to the β-positions of either an alkyl or an acyl radical would seem to call for a reinvestigation in the light of the present results.

It is evident from the above, that conclusions with regard to structure based on the interconversion of glycerol halohydrins into monomethyl ethers may be accepted as involving no migration of the methyl group.

Experimental

Preparation of Glycerol-α,α'-di-chlorohydrin.—One hundred grams of epichlorohydrin (b. p. 117°) was treated with approximately 125 cc. of concentrated hydrochloric acid. The latter was added in small quantities, the mixture being shaken and cooled throughout the addition. After standing for several hours at room temperature, the reaction product separated into two layers. The mixture was neutralized by washing with sodium bicarbonate solution, at which stage the lower layer was separated, dried over anhydrous sodium sulfate, filtered and fractionated, yielding 110 g. of glycerol-α,α'-di-chlorohydrin boiling sharply at 174–175°.

Methylation of Glycerol-α,α'-di-chlorohydrin.—Fifty grams of glycerol-α,α'-di-chlorohydrin was methylated in the usual manner, using 100 g. of silver oxide and 125 g.

---

[13] Gabriel and Ohle, *Ber.*, **50,** 804 (1917).

[14] Fischer, *ibid.*, **53,** 1621 (1920).

of methyl iodide. The reaction mixture was extracted three times with ether, the ether removed and the remaining product freed from unchanged α,α′-glycerol-dichlorohydrin by shaking vigorously several times with hot water. After drying with anhydrous sodium sulfate, careful fractionation yielded **21.4** g. of **glycerol-α,α′-di-chlorohydrin-**8-methyl ether, b. p. **157–159"**; n_D^{17} = **1.4550.**

Anal. Subs., **4.988** mg.: CO_2, **6.072** mg.; H_2O, **2.548** mg. Calcd. for $C_4H_8OCl_2$: C, **33.56;** H, **5.56.** Found: C, **33.20;** H, **5.71.**

Hydrolysis of **Glycerol-α,α′-di-chlorohydrin-β-methyl** Ether.—The method used for replacement of the two chlorine atoms by hydroxyl groups was essentially that used by Gilchrist and **Purves**,[5] but was modified to the extent that the hydrolysis of the di-acetate was carried out in acid instead of alkaline solution, as it had been previously **shown**[16] that the presence of dilute mineral acids has no influence on the methyl group.

Twenty and four-tenths grams of glycerol-α,α′-di-chlorohydrin-β-methyl ether was heated in a sealed tube with **29** g. of crystalline potassium acetate, dissolved in **50** cc. of 75% aqueous ethyl alcohol, for sixteen hours at 115–130°. The potassium chloride formed was removed by filtration and the filtrate containing the di-acetate **refluxed** for one hour with **100** cc. of 75% ethyl alcohol containing 3% of hydrochloric acid. The reaction mixture was neutralized with lead carbonate, the solution filtered and concentrated to a small volume. At this point considerable solid material separated out on cooling; this was removed by Ntration. The filtrate was further concentrated and then fractionated under reduced pressure, yielding a clear colorless liquid, b. p. 110° **(4** mm.), which on redistillation yielded pure **glycerol-β-**methyl ether, b. p. 123–125° **(13 mm.)**;[15] d_4^{17} = **1.1321;** n_D^{17} = **1.4485;** yield, **5.2** g., equal to 33% calculated on the glycerol-α,α′-di-chlorohydrin-β-methyl ether employed. The product was further identified by conversion into the *p*-nitrobenzylidene-glycerol-**β-methyl ether**[9] (m. p. 106°) as well as into the di-phenyl carbamate, m. p. **101°.** Mixed melting point determinations of these compounds with known samples showed no lowering of the melting point. A mixed melting point of the di-phenyl carbamate, as obtained above, with a known sample of the di-phenyl carbamate of **glycerol-α-methyl** ether (m. p. 118°) melted indefinitely at 90°.

No trace whatever was found of the corresponding isomeric glycerol-or-methyl ether.

Preparation of **Glycerol-α,β-di-chlorohydrin-α-methyl** Ether.—Twenty-three grams of **allyl** methyl ether (b. p. 42–43°) in which had been dissolved a small crystal of iodine was treated with a slight excess of chlorine at 0°. The uncombined halogen was removed by bubbling dry air through the reaction mixture, the latter was thoroughly washed by shaking with water, the lower layer separated, dissolved in ether and dried over anhydrous sodium sulfate. Fractionation of this yielded **20.4** g. of glycerol-α,β-di-chlorohydrin-α′-methyl ether, b. p. 153–157°; n_D^{17} = **1.4489.** During the distillation hydrogen chloride was formed in slight amount due to a small amount of secondary decomposition.

Anal. Subs., **5.471** mg.: CO_2, **6.669** mg.: H_2O, **2.735** mg. Calcd. for $C_4H_8OCl_2$: **C, 33.56;** H, **5.56.** Found: C, **33.25;** H, 5.59.

Hydrolysis **of Glycerol-α,β-di-chlorohydrin-α-methyl** Ether.—The replacement of the chlorine atoms by acetyl groups was a much more difficult operation than in the case of the corresponding glycerol-α,α′-di-chlorohydrin-β-methyl ether. In marked contrast to the behavior of the latter with potassium acetate in aqueous alcoholic solution, it was found that glycerol-α,β-di-chlorohydrin-α′-methyl ether yielded a large amount of unsaturated derivatives, a reaction apparently common to organic products

---

[15] Hill, Whelen and Hibbert, THIS JOURNAL, 50, **2235 (1928).**

containing chlorine atoms attached to adjacent carbon atoms. Substitution of sodium formate for potassium acetate led to the same result. It was found, however, that the desired diacetate could be obtained (although in low yields) by heating **20.4** g. of glycerol-α,β-di-chlorohydrin-α′-methyl ether with **29** g. of fused potassium acetate and **30** cc. of glacial acetic acid under pressure at 165° for sixteen hours. The crude reaction product had a dark brown color. It was filtered from the solid material, the filtrate neutralized with solid potassium carbonate, again filtered and the filtrate concentrated under reduced pressure to a small volume. Further filtration and fractionation of the filtrate yielded **4.2** g. of a clear colorless liquid, b. p. 215–225°. Three grams of this material was hydrolyzed by refluxing for one hour with **25** cc. of 75% aqueous ethyl alcohol containing **3**% of hydrochloric acid. After neutralization with lead carbonate, filtration and concentration, the residual oil on distillation yielded **1.2** g. of glycerol-α-methyl ether; b. p. 111–112° **(13** mm.); d_4^{17} = **1.1189;** n_D^{17} = **1.4445.** Its identity as pure glycerol-a-methyl ether was further established by its conversion into the di-phenyl carbamate, m. p. **117"** C.[9] **A** mixed melting point of this material with a known sample showed no lowering, while a mixed melting point with the di-phenyl carbamate of glycerol-8-methyl ether melted indefinitely at **93°.**

Summary

1. Glycerol-α,α′-di-chlorohydrin on methylation and conversion of the α,α′-dichloro-β-methyl ether into the acetate, followed by saponification, yields only glycerol-β-methyl-ether.

2. Glycerol-α,β-di-chlorohydrin-α′-methyl ether on conversion into its acetate, followed by saponification, yields only glycerol-a-methyl ether.

3. Previous work in this field, pointing to the probability of the migration of a methyl radical in the conversion of glycerol-α,α′-di-chlorohydrin-β-methyl ether into the acetate and subsequent hydrolysis of the latter is based on the mistaken identity of the resulting product as glycerol-α-methyl ether.

4. The bearing of these results on the methylation of glycerol and carbohydrate derivatives is pointed out and the importance of the pure α- and @-glycerohnethyl ethers as "type substances" further confirmed.

MONTREAL, CANADA

NOTES

The Identification of **Ortho-, Meta-** and Para-Hydroxybenzoic Acids.—It was found necessary, recently, to isolate, purify and identify small amounts of *o*-, *m*- and *p*-hydroxybenzoic acids.

Lyman and Reid[1] have recommended the p-nitrobenzyl esters as suitable compounds by means of which these hydroxy acids can be identified. These investigators converted the acids into their sodium salts and heated these, dissolved in a mixture of water and alcohol, with p-nitrobenzyl bromide. We obtained unsatisfactory results by the use of this method since it was found that the esters, as soon as they are formed, react to some extent with p-nitrobenzyl bromide to form the p-nitrobenzyl

---

[1] Lyman and Reid, THIS **JOURNAL, 39,704 (1917).**

ethers, that is, the dinitrobenzyl derivatives of the hydroxy acids. In fact the substance described by Lyman and Reid as the *p*-nitrobenzyl ester of p-hydroxybenzoic acid was, in reality, the dinitrobenzyl compound.

The esters, or mononitrobenzyl compounds, are very soluble in organic solvents and hence are difficult to purify, but the dinitrobenzyl derivatives are much less soluble and can be recrystallized readily from acetone. The method was now modified in such a way that the formation of the dinitrobenzyl products was favored. As a result not only were compounds formed which could be recrystallized with less loss of material, but since the molecular weight of the dinitrobenzyl derivative is considerably higher than that of the mononitrobenzyl compound, a larger amount of material, in the case of the former substance, could be obtained from a given weight of the hydroxy acid. Furthermore, by the use of the dinitrobenzyl derivatives, it is possible to separate a mixture of two isomeric hydroxybenzoic acids; the derivative of the p-hydroxy acid is quite insoluble in acetone, that of the meta acid more soluble while the ortho isomer is fairly soluble.

The di-*p*-nitrobenzyl compounds were obtained in the following manner: 1.25 g. of p-nitrobenzyl bromide was dissolved in 10 cc. of pure acetone and a solution prepared from 0.35 g. of the hydroxy acid, **0.3** g. of sodium hydroxide crystals ($NaOH + H_2O$)[2] and 4 cc. of water was added. The mixture was refluxed for two hours. In the case of the p-hydroxy acid the dinitrobenzyl derivative separated in crystalline form from the hot reaction mixture; from the m- and o-hydroxy acids oils were obtained which solidified when cooled. The products were treated with 5 cc. of 10% sodium hydroxide and then filtered. The dinitrobenzyl compounds remained undissolved while the alkaline filtrate yielded, upon acidification, a small amount of the ether-acid. After three recrystallizations from acetone the derivatives were obtained in a nearly colorless state.

TABLE I

DI-*p*-NITROBENZYL DERIVATIVES OF HYDROXYBENZOIC ACIDS

	M. p., °C.	Analysis (Dumas), % Calcd. for $C_{21}H_{16}O_7N_2$	Found
o-Hydroxy[a]	137–139	N 6.86	6.50
m-Hydroxy[b]	142–144	N 6.86	6.86
p-Hydroxy[c]	196–197	N 6.86	6.83

[a] Readily soluble in hot acetone and somewhat soluble in the cold solvent, insoluble in ether and soluble in hot benzene.

[b] The solubilities are intermediate between those of the ortho and para isomers.

[c] Quite insoluble in hot acetone, ether and benzene.

The mononitrobenzyl derivatives, that is, the p-nitrobenzyl esters, were prepared as follows: 1.4 g. of the hydroxy acid and 0.55 g. of sodium hydroxide crystals were dissolved in 5 cc. of water. After the addition of 15 cc. of pure acetone, 2.15 g. of p-nitrobenzyl bromide was added in

---

[2] An equivalent amount of potassium carbonate may be used instead.

small portions during the course of one-half hour, the material having been refluxed during this period. The mixture was heated for an hour longer, then cooled, diluted with water, acidified with hydrochloric acid and the precipitated material filtered. The latter was treated with 5% sodium hydroxide and filtered to remove the dinitrobenzyl derivative and other alkali-insoluble compounds. The alkaline filtrate was acidified and the precipitate filtered. The product was dried and then dissolved in a very small amount of hot acetone. Water was added until the solution became turbid. When cooled the mononitrobenzyl derivative separated in crystalline form.

TABLE II

p-NITROBENZYL ESTERS OF HYDROXYBENZOIC ACIDS[a]

	M. p., °C.	Analysis (Dumas), % Calcd. for $C_{14}H_{11}O_5N$	Found
o-Hydroxy[b]	97– 98	N 5.12	5.15
m-Hydroxy[c]	106–108	N 5.12	5.23
p-Hydroxy[d]	180–182	N 5.12	5.22

[a] These compounds are all very soluble in cold acetone and alcohol.

[b] Lyman and Reid, THIS JOURNAL, 39, 710 (1917), obtained this substance but published no analytical results.

[c] Lyman and Reid, *ibid.*, 39, 710 (1917).

[d] Lyman and Reid, *ibid.*, 39, 711 (1917), obtained a compound which they supposed to be the p-nitrobenzyl ester of p-hydroxybenzoic acid; the substance melted at 198.5". This compound was undoubtedly the dinitrobenzyl derivative.

The p-nitrobenzyl ethers of the hydroxy acids were obtained as follows: 0.5 g. of the dinitrobenzyl derivative was hydrolyzed with **3** g. of potassium carbonate dissolved in 30 cc. of 50% alcohol. The alcohol was evaporated on a steam-bath and the aqueous mixture filtered from p-nitrobenzyl alcohol. The alkaline filtrate was acidified and the precipitated material recrystallized from a small amount of acetone.

TABLE III

p-NITROBENZYL ETHERS OF HYDROXYBENZOIC ACIDS

	M. p., °C.	Analysis (Dumas), % Calcd. for $C_{14}H_{11}O_5N$	Found
o-Hydroxy[a]	166–168	N 5.12	5.20
m-Hydroxy[b]	193–196	N 5.12	5.25
p-Hydroxy[c]	259–261	N 5.12	5.05

[a] This compound is soluble in hot acetone and alcohol.

[b] This substance is somewhat soluble in hot acetone and alcohol.

[c] Inasmuch as the dinitrobenzyl derivative of the *p*-hydroxy acid is insoluble in dilute alcohol, it is hydrolyzed into the ether much more slowly than the other isomeric dinitrobenzyl compounds. The ether is practically insoluble in hot acetone and hot alcohol.

CONTRIBUTION FROM THE
COLLEGE OF PHARMACY OF THE
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

F. F. BLICKE
F. D. SMITH

RECEIVED JANUARY 31, 1929
PUBLISHED JUNE 5, 1929

Esters of Dimethylethylacetic Acid.—In the course of an investigation being carried on in this Laboratory we had occasion to synthesize several esters of dimethylethylacetic acid. This acid was prepared by treating *tert.*-amylmagnesium chloride with carbon dioxide; esterification was brought about by refluxing the acid and the required alcohol with sulfuric acid as catalyst.

Tert.-amyl chloride was prepared in the following manner. Four thousand cc. of concentrated hydrochloric acid was added, during fifteen to twenty minutes, with mechanical stirring, to 2500 g. of *tert.*-amyl alcohol[1] contained in a 12-liter earthenware crock. The mixture warmed up to 45°; stirring was continued for four hours. The upper layer, *tert.*-amyl chloride containing some unchanged alcohol, was transferred to a 12-liter flask and saturated with dry hydrogen chloride in the presence of anhydrous calcium chloride, the mixture being mechanically stirred throughout the process. Saturation required one and one-half hours; the mixture warmed up to 50°. The calcium chloride was then removed and the *tert.*-amyl chloride mixture was refluxed for an hour. After standing over anhydrous sodium carbonate for twenty-four hours the product was filtered. Twenty cc. of dimethylaniline was then added and the product distilled through a 50-cm. fractionating column. There is continuous evolution of hydrogen chloride during distillation if dimethylaniline is not added. The *tert.*-amyl chloride boiled at 84–86°; the yield was 1960 g., or 65% of the theoretical amount.

Dimethylethylacetic acid was prepared in 60% yield by treating *tert.*-amylmagnesium chloride with carbon dioxide. Our procedure was patterned after that of Puntambeker and Zoellner[2] for the preparation of trimethylacetic acid. The ether from which the dimethylethylacetic acid had been extracted by means of sodium hydroxide solution, by the above directions, contained two by-products—*tert.*-amyl alcohol (b. p. 99–103°, n_D^{23}, 1.4035) and a camphoraceous smelling liquid (b. p. 164–167.5"; n_D^{22}, 1.4335; molecular weight in acetone, 183) which we have not yet investigated.

The esters are colorless liquids. The methyl, ethyl and n-propyl esters have menthol–peppermint odors; the n-butyl, n- and iso-amyl esters have but little odor. The refractive indices were determined at 25.0 ± 0.1" by means of an Abbé refractometer; the densities were determined at 25.00 ± 0.02° by means of a pycnometer of about 8-cc. capacity. The weights used in the density calculations were corrected for buoyancy. The boiling points were determined by means of Anschütz thermometers (stem wholly immersed in vapor) which had been standardized by the U. S. Bureau

---

[1] Kindly furnished by the Sharples Solvents Corporation.

[2] Puntambeker and Zoellner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 8, 104 (1928).

of Standards. The molecular weights were calculated using the Lorentz–Lorenz formula. Considerable difficulty was experienced in analyzing these esters, especially the lower ones, low results being obtained repeatedly. Correct results were finally obtained in all cases except that of the methyl ester by using a quartz combustion tube and high temperature.

TABLE I

ESTERS OF DIMETHYLETHYLACETIC ACID

Ester	B. p., °C. (746 mm., corr.)	n_D^{25}	d_4^{25}	Mol. wt. Calcd.	Mol. wt. Found	Analyses Calcd. C, %	Analyses Calcd. H, %	Analyses Found C, %	Analyses Found H, %
Methyl	125 –125.5	1.3991	0.8943	130	134	64.6	10.8	61.0	10.7
								62.8	7.7
Ethyl[a]	141.8–142.2	1.3989	.8601	144	145	66.6	11.2	66.4	11.1
n-Propyl	164 –164.4	1.4040	.8575	158	159	68.4	11.5	68.1	11.4
n-Butyl	184 –184.7	1.4098	.8566	172	173	69.7	11.7	71.0	11.5
n-Amyl	202.5–203.5	1.4140	.8544	186	187	70.9	11.9	71.0	11.8
Iso-Amyl	192.5–196.5	1.4128	.8533	186	187	70.9	11.9	70.6	11.7

[a] Bouveault and Blanc, Bull. *soc. chim.*, [3] 31, 749 (1904), report boiling point as 141–142° and d_4^0 as 0.883.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
MIDDLEBURY COLLEGE
MIDDLEBURY, VERMONT

B. B. CORSON
J. S. THOMAS
D. D. WAUGH

RECEIVED FEBRUARY 11, 1929
PUBLISHED JUNE 5, 1929

Reaction of Alizarin and Mercuric Acetate.—The observation here reported was made some six years ago. Since the work is not to be continued, the facts obtained are presented as being of possible interest in anthraquinone chemistry.

Alizarin when heated with excess mercuric acetate gave large amounts of mercurous acetate, indicating an oxidation of the alizarin. The product contained organic mercury. Five runs with varying concentrations and times of heating varying from 30 to 100 hours gave almost identical results. The organic product appeared to be acetoxymercurydihydroxyalizarin. The following average analyses were obtained on the products from the five runs.

Anal. Calcd. for $C_{16}H_{10}O_8Hg$: Hg, 49.8. Pound: 49.5, 50.0, 49.8, 49.7, 49.7.

Treatment of the product with hydrochloric acid gave a yellow-red dye with properties similar to those of alizarin.

The mercury compound when treated with the amount of standard sodium hydroxide corresponding to the four hydroxyls gave a bluish-red solution. The solution at 20° then contained 0.2 g. per 100 cc. Warming the solution changed the color to red and precipitated some material which dissolved again on cooling. Both the cold and hot solutions were neutral to litmus.

The positions of the groups in the mercurated product were not determined. The results of other oxidation and substitution reactions on alizarin would make it appear probable that the product was 1,2,5,8-tetrahydroxy-4-acetoxymercuri-anthraquinone. Treatment of this product with halogens should give interesting halogenated tetrahydroxyanthraquinones.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
FRANK C. WHITMORE
G. J. LEUCK

RECEIVED MARCH 4, 1929
PUBLISHED JUNE 5, 1929

The Reaction of Mercuric Acetate with *p*-Bromodiethylaniline.—The present observations are published because of their wide divergence from the results obtained with closely analogous substances. Dialkylanilines, including dimethyl, diethyl, di-n-propyl, di-n-butyl, methylethyl, and ethylbenzyl, react readily with mercuric acetate to give products containing acetoxymercuri groups in the para position.[1] If the para position is occupied, mercuration would be expected to take place in one of the free ortho positions. This proved to be the case with *p*-bromodimethylaniline, which gave an excellent yield of the ortho mercurated product.[2] At the time that work was done, attempts were made to extend it 'to the homologous dialkylanilines. Contrary to expectations, this proved to be impossible. The experiments have been repeated many times since under a great variety of conditions, but the results have been consistently negative. No organic mercury compound has been obtained.

The attempts at mercuration of p-bromodiethylaniline were carried out in 95% alcohol, 50% alcohol, glacial acetic acid, 50% acetic acid, ether, water and without a solvent. The temperature was varied from 0° to the boiling point of the solvent used and the times from a few hours to weeks. The concentrations of the reactants were varied over a wide range. In all experiments similar results were obtained; the products were unchanged material, mercurous acetate and unmanageable oxidation products.

UNIVERSITY OF MINNESOTA AND
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
FRANK C. WHITMORE
A. R. CADE
G. J. LEUCK

RECEIVED MARCH 6, 1929
PUBLISHED JUNE 5, 1929

---

[1] Whitmore, Hanson and Carnahan, THIS JOURNAL, 51, 894 (1929).

[2] Whitmore, *ibid.*, 41, 1841 (1919).

NEW BOOKS

Matter, Electricity, Energy. The Principles of Modern **Atomistics and** Experimental Results of Atomic Investigation. By WALTER GERLACH, University of Tiibingen. Translated from the second German edition by Francis J. Fuchs, Ph.D., St. John's College. D. Van Nostrand Company, Inc., 8 Warren Street, New York, 1928. xii + 427 pp. 119 figs. 16 × 23.5 cm. Price, $6.00.

Since the first edition of this work was published in German, and reviewed in THIS JOURNAL, 46, 517 (1924), experimental advances in atomistics have all but kept pace with the unprecedented development of the theoretical side of the subject. Among newer subjects discussed here will be found Atomic Rays and the Compton Effect but, in general, no great effort appears to have been made to bring the book really up to date. It is gratifying that a book as good as this, yet which does not follow the lines either of an orthodox text or a reference work, can appear in translation. It should be useful to many students of modern physical developments.

NORRIS F. HALL

Collection of Czechoslovak Chemical Communications. Edited and published by E. VOTOČEK AND J. HEYROVSKÝ under the patronage of the Bohemian Royal Society of Sciences. 1929. Year 1, No. 1, January. Printed by "Politika," Prague. Agent U. S. A., Dr. N. V. Emelianoff, Havemeyer Hall, Columbia University, New York City. Subscription price, U. S. A., $5.00.

It appears that the limited knowledge of Czech outside of Bohemia has, on the one hand, forced the chemists of that country to publish their chief works in foreign journals and, on the other, has resulted in many important contributions remaining untranslated in the archives of the Czech learned societies and institutions. The Editors have founded this journal to remedy these difficulties by publishing in full the more important contributions of their countrymen in the field of "pure" chemistry, provided they have not been published previously in any widely known language. This journal will also include a bibliography of all publications of Czechoslovak chemists, as well as reviews of their books.

This first issue contains four articles, one on inorganic, one on physical-analytical and two on organic chemistry. One of these articles is in English; the other three are in French.

ARTHUR B. LAMB

Leçons sur la **Chimie Générale.** (Lessons in General Chemistry.) By RENÉ DUBRISAY, Professor at the National School of Bridges and Roads. Gauthier–Villars et Cie., 55 Quai des Grands-Augustins, Paris, France, 1929. vi + 246 pp. 16.5 X 25.5 cm. Price, $2.98.

This is a short course of lectures, intended as a second trip over the chemical field for students of engineering who have already studied descriptive chemistry. The author shows the application of physical chemistry to many industrial processes. The work is divided into an introduction and four parts which deal, respectively, with atomistics, thermodynamics, kinetics and equilibria, electrochemistry and surface chemistry. In part one, the treatment is rather too brief to be satisfactory but the material seems well selected. Figures one and two are misleading. In part two the discussion of oxidative catalysis and the drying of oils is interesting. In developing the fundamental equations for chemical equilibria and the phase rule, a rather detailed analytical discussion is used, in which the Gibbs Zeta-function is emphasized and this function is called the "thermodynamic potential" while the Psi-function is called the "free energy." A rather extensive use of phase diagrams is made in the section on metallography. In particular the T–X diagram for the system Cu–Sn is presented in considerable detail. In the section on ionization the hypothesis of Arrhenius is uncritically applied to strong electrolytes. The electrochemical section is very brief and modern solution theory finds no place in it. In the section on surface chemistry the Gibbs Zeta-function is used once more in developing the adsorption equation of Preundlich. Chapters on clays and cements conclude the book.

The style is clear and extremely concise and the methods of selection and presentation testify to the intelligence both of the lecturer and of French students of engineering.

NORRIS F. HALL

The Fundamentals of Chemical Thermodynamics. Part I. Elementary Theory and Applications. BY J. A. V. BUTLER, D.Sc., Lecturer in Chemistry in the University of Edinburgh. Macmillan and Co., Ltd., St. Martin's Street, London W.C. 2, England, 1928. xi + 207 pp. 51 figs. 12.5 × 19.5 cm.

In response to the need "of an elementary introduction to the subject which shall stress the underlying principles and at the same time give due attention to their applications" the author has "tried to present the subject in a logically precise, yet simple form, having in mind not only the student who intends to specialize in Physical Chemistry, but also that class of chemistry students which has only a very moderate knowledge of mathematics and little sympathy with mathematical methods." This volume is based mainly on cyclic processes, and ,comprises nine chapters, as follows: first law; second law; changes of state; solutions; homogeneous-gaseous reactions; the galvanic cell; electrode potentials; concentration cells and activities; electrolysis. To each chapter is appended a group of examples, taken from recent papers and not obsolete data copied from other textbooks. In his purpose the author has, I think, succeeded perhaps as well as is possible within the compass of 200 small pages; but one wonders whether it is not rather condensed nourishment, except for the few with thoroughly analytical minds, and whether for the others the thermodynamic pill must not be gilded with a more discursive treatment, with a large use of analogies, with philosophy and even with humor, if it is to produce any beneficial effect upon the patient. Indeed, I fear that it is nearly impossible to write a good brief exposition of thermodynamics—unless as a summary which would be amplified greatly by the teacher in class—which will appeal with any degree of success to the average student of chemistry; he should, however, find the texts written within the last fifteen years much less unattractive and less incomprehensible than the older books, many of them written by men who allowed but little real chemistry to slip in.

J. JOHNSTON

Introduction to Modem Physics. BY F. K. RICHTMYER, Professor of Physics at Cornell University. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1928. xv + 596 pp. 169 figs. 15 X 23.5 cm Price, $5.00.

This fairly large and leisurely book has already found a warm welcome among students and teachers of physics, and should equally please those chemists and other non-physicists who are forced by interest or necessity to follow as best they can the brilliant pageant of modern physical advance. Intending neither to produce a textbook of physics in general nor a work of reference, the author has been able to select his material with a relatively free hand.

His method is as follows. First, the whole history of physics is surveyed in a section of about seventy pages, which brings the account to the last decades of the nineteenth century. The electromagnetic theory of light is then expounded, followed by the story of the photoelectric effect from Hertz to Ives. Next is a long section devoted to thermal radiation, the origin of the quantum theory and its application to specific heats. Then comes a study of series relations in line spectra, the development of the nucleus-atom and its introduction into spectral theory. The arrangement of electrons in atoms is discussed in connection with both static and dynamic models and, finally, a complete survey of the history and present status of x-rays introduces a last chapter on the nucleus and radioactivity. Appendices contain valuable tables. This choice of subjects permits the author to dwell with each in turn, to regard it from different points of view, to raise interesting side issues and to show the essentially continuous and even recurrent character of the evolution of physics. Of course, not everything "modern" finds a place—there is no general and little special relativity, no matrix—or wave—mechanics, no ultrasonics, no electron tubes. There is even no treatment of sound, or of light as such, or of ordinary mechanics.

Therefore let the reader or purchaser of this book understand just what he is getting: a readable, solid and thorough *introduction* to those parts of physics which by common consent are regarded as most interesting. The diagrams have evidently been very carefully prepared..

A list of minor errors has been sent to the author.

NORRIS F. HALL

A Guide to the Literature of Chemistry. By E. J. CRANE, Editor of Chemical *Abstracts,* and AUSTIN M. PATTERSON, Professor of Chemistry, Antioch College, Formerly Editor of *Chemical Abstracts,* John Wiley and Sons, Inc., New York, 1927. ix + 438 pp. Illustrated. 15.5 X 23.5 cm. Price $5.00.

The literature of chemistry, including those closely related subjects which engage the chemist's attention, is more extensive than that of any other branch of science, and there is probably no other field of pure or applied science in which consultation of the existing literature is more highly essential. Even in routine work some contact with published information is desirable, while in investigation the use of existing records is imperative. Every research should begin with the literature of the subject; frequently it may end there.

The student of chemistry is given detailed instruction in the manipulation of the apparatus he is to use; but too frequently he is given only superficial instruction, or none at all, in the method of approaching the literature, though indexes and library catalogs are tools, also, and the technique of using them properly does not come intuitively. But while there are many books for the chemist in the laboratory, there have been very few for the chemist in the library. A pioneer work is the pamphlet by Miss Marion Sparks,[1] who up until her recent untimely death gave instruction in chemical literature to students at the University of Illinois. In his valuable guide to research in organic chemistry, Dr. E. E. Reid[2] of Johns Hopkins University wisely devoted approximately one-third of the space to libraries and literature. A recent work by Dr. M. G. Mellon,[3] based on instruction at Purdue University, gives considerable attention to actual library problems and assignments.

There are a few other brief guides, but the book by Crane and Patterson presents the maximum cross-section of the literature. Its content cannot be reviewed in detail here, but, in general, it surveys the important classes of literature (such as books, periodicals, patents, and trade literature), and indicates the approach thereto by means of the available tools (such as indexes, abstracts, reviews and bibliographies). Supplementing the

---

[1] Sparks, "Chemical Literature and Its Use," privately printed, Urbana, Ill., 2d. ed., 1921.

[2] Reid, "Introduction to Organic Research," D. Van Nostrand Co., New York, 1924.

[3] Mellon, "Chemical Publications, Their Nature and Use," McGraw-Hill Book Co.. New York, 1928.

general instruction, there are useful features of rather special nature, for example, the principles of indexing, and the transliteration of Russian names.

The procedure for systematic searching of the literature is well outlined, and at least a part of the instruction given in the book should be incorporated in every formal course in chemistry, to the end that every chemist shall be able to find information in print, and to record it with such accuracy that his references will enable him, or anyone else, to find the material again. In addition to its value for actual study, the volume offers a large amount of reference material—mainly in the form of lists. These include a bibliography of chemical literature and lists of abbreviations, libraries, periodicals, societies, publishers and books—all considered from the viewpoint of the chemist. Some of these lists are of more ephemeral nature than the rest of the book and they will need occasional revision. At present, they are of enormous reference value and the book should be available for consultation in every laboratory which does anything beyond the most ordinary routine work.

Having been invited to review this "Guide" so long after its appearance, the present reviewer accepted because the book continues to justify its existence and (where used as it was intended to be) to evoke enthusiasm as evinced by the following comment in a letter from a personal friend who has had wide experience in the use of technical literature: "What a beautiful piece of work Crane and Patterson have done in their Literature of Chemistry. I admire it more and more every time I use it."

E. H. McClelland

Richter-Anschiitz Chemie der Kohlenstoffverbindungen oder **Organische** Chemie. (Organic Chemistry or the Chemistry of the Compounds of Carbon.) Edited by Dr. Richard Anschütz. Vol. I. Aliphatic Compounds. By Dr. Fritz Reindel, Lecturer in Organic Chemistry at the Technical High School of Munich, Twelfth edition. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 4, Leipzig C 1, Germany, 1928. xvi + 882 pp 18 figs. 16 × 24 cm. Price, unbound, M 57; bound, M 59.

After an interval of nineteen years, during which many of the friends of the "Richter–Anschiitz" began to fear that its faithful editors had succumbed to an ever-growing mass of facts, this first volume of the twelfth edition has appeared—thoroughly up to date, cleanly printed on good paper, therefore just as reliable and much more attractive than any of the preceding editions.

Since the plan of this text has remained the same throughout its long history, the differences between successive editions give a good indication of the subjects which from time to time have engrossed the interest of investigators in organic chemistry. In the present edition the sections dealing with alcoholic fermentation, polysaccharides, proteins, porphyrins, bile-acids, sterins and enzymes have been completely rewritten and considerably expanded. These sections contain the major changes from the eleventh edition but the entire text has been thoroughly revised and there is hardly a page in which no new material has been incorporated. Both the editors and the publishers are to be commended for the high quality of the present volume. It deserves to win a host of new friends for an old favorite.

E. P. KOHLER

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. IX. **Edited by JAMES B. CONANT, with ROGER ADAMS, H. T. CLARKE, HENRY GILMAN, C. S. MARVEL and FRANK C. WHITMORE. John Wiley and Sons, Inc., 440 Fourth Avenue, New York,** 1929. **v** + 108 **pp. 1 fig. 15.5 × 23.5 cm. Price, $1.75.**

The ninth annual volume of Organic Syntheses arrived on time, with a long list of contributors of whom many—perhaps most—appear for the first time in this edition. Evidently the little guide is enjoying increasing favor not only with those who look to it for assistance, but also with those who have had occasion to devise new methods or carefully study old ones for the preparation of organic compounds. The list of substances dealt with in the present volume is as follows: Acid ammonium o-sulfobenzoate, dkalanine, ammonium salt of aurintricarboxylic acid, anisole, benzoylpiperidine, p-bromophenacyl bromide, o-bromotoluene, n-butyl carbamate, n-butyl p-toluenesulfonate, n-butyryl chloride, o-chlorobenzoyl chloride, cyanoacetamide, ethyl cinnamate, hydrocinnamic acid, iodobenzene, levulinic acid, 1-menthone, mercury diphenyl, methylene bromide, monochloromethyl ether, 0-naphthol phenylaminomethane, o-nitroaniline, nitrostyrene, pentamethylene bromide, y-phenoxypropyl bromide, phloroglucinol, pyrrole, o-sulfobenzoic anhydride, *ac.*-tetrahydro-β-naphthylamine.

E. P. KOHLER